Results and Discussion

1. Chlorpyrifos

1.1. Effect of storage stability on chlorpyrifos 48% EC content

The data from Table 3 and Fig. 1 showed that the effect of storage at 54 ±2 ^{0}C on three commercial chlorpyrifos formulations (manufactured from various companies).

Chlorpyrifos has not been changed by storage at 54 ±2 °C for 1, 3, 7, 14, 21 days, where chlorpyrifos content before storage was 47.02, 47.09, and 47.2% for source I, II, and III respectively.

Results indicated that chlorpyrifos content after storage for 14 days was 46.1, 45.38, and 45.81% for source I, II and III respectively, and it has percentage of loss 1.96, 3.63, and 2.94% for source I, II and III respectively.

Also chlorpyrifos content after storage for 21 days was 45.21, 44.99, and 45.43% for source I, II and III respectively, and it has percentage of loss 3.85, 4.46, and 3.75% for source I, II and III respectively. The calculated t_{95} for chlorpyrifos from source I, II, and III was 27.47, 23.61, and 28.19 days respectively.

According to FAO specifications and evaluations (2008) for chlorpyrifos mentioned that the content of chlorpyrifos after storage at 54 ±2 °C for 14 days should not be lower than 95% relative to the content of chlorpyrifos before storage, and this achieved in this studying according to Table 1.

Chlorpyrifos was more stable after storage at room temperature for 1, 2, 4, 6, 8, 10, 12 weeks, and Table 4 and Fig. 2 showed that chlorpyrifos content after storage for 12 weeks was 46.025, 45.69, and

46.11% for source I, II, and III respectively, and it has percentage of loss was 2.12, 2.97 and 2.31% for source I, II, and III respectively. The calculated t_{95} for chlorpyrifos from source I, II, and III was 201.46, 142.78, and 184.43 days respectively.

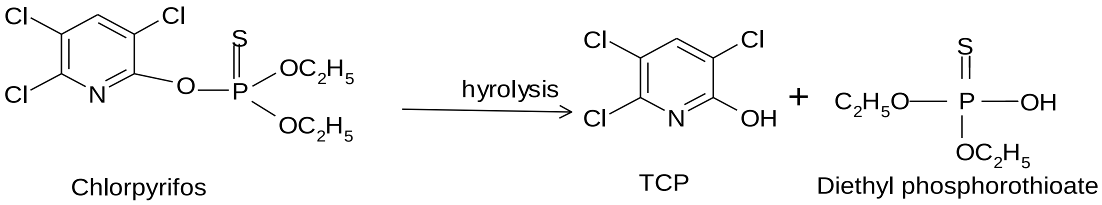
Whereas the stability of chlorpyrifos after storage at 72 ±2°C for 1, 2, 3, 4, 5 days was less stable from storage at room temperature and 54 ± 2 °C. The data from Table 5 and Fig. 3 showed that chlorpyrifos content after storage at 72 ±2 °C for 5 days was 41.79, 41.30, and 41.35%, and it has percentage of loss 11.12, 12.30, and 12.39% for source I, II, and III respectively. The calculated t_{95} for chlorpyrifos from source I, II, and III was 2.18, 1.95, and 1.94 days respectively.

The previously mentioned results clearly showed that the rate of degradation of the three chlorpyrifos formulations under investigation was influenced by change in temperature degrees and long period of storage. In general increasing temperature degrees increased the rate of degradation.

The samples of chlorpyrifos were analyzed after storage by GC-MS to identify some degradation compounds, and from the analysis of our samples by using GC-MS found that the characteristic ions at m/z 351, 198.5, 171, and 314 were molecular ions of chlorpyrifos, TCP, diethyl phosphorothioate and O,O-diethyl-O-3,6-dichloro-2-pyridyl phosphorothioate. The data in Fig. (4, 5) showed that mass spectrum and possible degradation pathways of chlorpyrifos.

The degradation pathways of chlorpyrifos can be explained that the primary degradation product of chlorpyrifos can be explained by both hydrolysis and photolysis. The analysis of our samples by using GC-MS found that chlorpyrifos can be hydrolysed to 3, 5, 6- trichloro -2-

pyridinol (TCP), also by electron impact found to give compounds 1,2 which in accordance with the hydrolysis. Phosphorus oxygen bond was cleaved to generate TCP and diethyl phosphorothioate, these results were in line with [5], and this can be shown according to the following equation.



The mass spectrum and mass fragmentation of TCP can be shown in Fig. (6, 7).Also the mass spectrum and mass fragmentation of diethyl phosphorothioate (2) can be shown in Fig. (8, 9).

There is another possible degradation pathway of chlorpyrifos and from Fig. 5 can be observed compound no. (3) which formed from chlorpyrifos by loss chlorine atom and give O,O-diethyl-O-3,6-dichloro-2-pyridyl phosphorothioate (3), and from GC-MS we found that ion peak at m/z 314 [M-2] was molecular ion of compound no. (3), and also Fig. (10, 11) showed that mass spectrum and mass fragmentation of compound no. (3).

According to [77] chlorpyrifos is thermally sensitive to temperature over 50 °C and this achieved in this study.

The obtained results were agreement with [49] found that chlorpyrifos is more stable than pirimiphos- methyl after storage at 54 °C ±2 for 14 days.

Also results were agreement with [33] as they reported that the chemical decomposition of chlorpyrifos was higher under tropical storage (54-72°C) than roof and shelf storage and increased by increasing the storage period.

The previously result showed that chlorpyrifos may affected by many factors such as chemical structure, photodecomposition, hydrolysis, oxidation, and isomerization this are agreement with [78].

1.2. Effect of storage stability on the formation of sulfotep

The data from Table 6 showed that the effect of storage on the amount of sulfotep in chlorpyrifos 48% EC from three different manufactured sources at 54 ± 2 °C for 1, 3, 7, 14, 21 days, and at 72 ± 2 °C for 1, 2, 3, 4, 5 days. The amount of sulfotep in chlorpyrifos formulations was 1.24, 7.18, and 0.27 g/kg for source I, II, and III respectively before storage.

Results indicated that the amount of sulfotep after storage at 54 ± 2 °C for 14 days was 1.24, 7.74, and 0.39 g/kg of chlorpyrifos for source I, II, and III respectively, where the maximum level of sulfotep in chlorpyrifos emulsifiable concentrate is 0.3% of chlorpyrifos content as from the obtained results the maximum level was 1.24, 1.28, and 1.28 g/kg for source I, II, and III respectively.

Also the amount of sulfotep after storage for 21 days was 1.24, 8.87, and 0.33 g/kg of chlorpyrifos for source, I, II and III, respectively, where the maximum level of sulfotep was 1.28, 1.26, and 1.27 g/kg for source I, II, and III respectively.

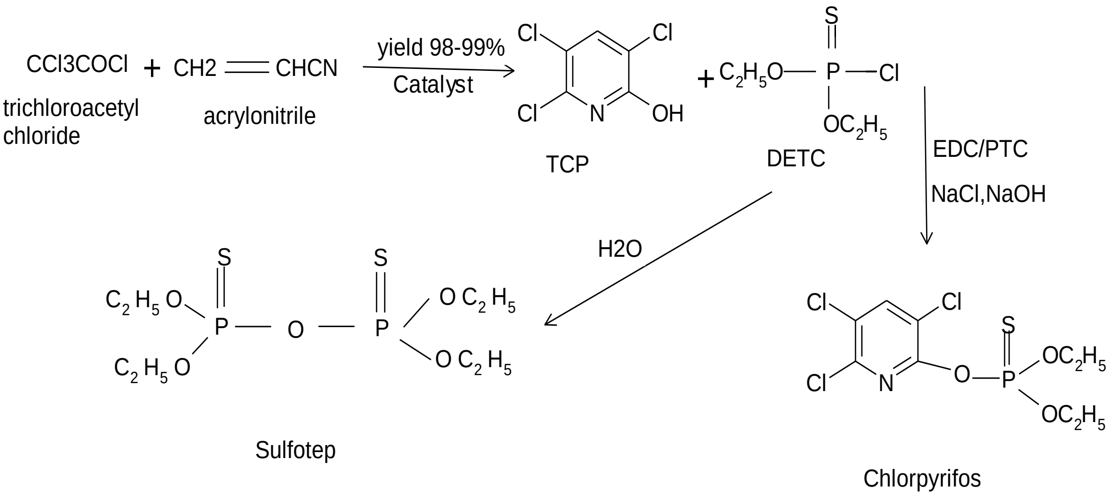
Also the data from Table 6 indicated that the amount of sulfotep after storage at 72 ± 2 °C for 5 days was 1.17, 8.10, and 0.36 g/kg for source I, II, and III respectively, where the maximum level of sulfotep was 1.18, 1.17, and 1.17 g/kg for source I, II, and III respectively.

The results from Table 7 showed that the amount of sulfotep after storage at room temperature for 12 weeks was 1.18, 7.41, and 0.27 g/kg of chlorpyrifos, where the maximum level of sulfotep was 1.30, 1.28 and 1.29 g/kg for source I, II, and III respectively.

The previously mentioned results clearly showed that the amount of sulfotep didn't affect by long period of storage and storage at high temperature, and also the amount of sulfotep from source I and III was in allowed limits according to [1], but the amount of sulfotep from source II was more than the allowed limits and that was found before storage and after storage at room temperature, 54 ±2 °C and 72 ±2 °C.

The previously mentioned results clearly showed that the amount of sulfotep in chlorpyrifos formulation from three sources was affected by many factors such as manufacturing process and sources of starting materials, and also the presence of sulfotep in technical chlorpyrifos. By the analysis of technical chlorpyrifos from three sources (manufactured from various companies) to identify and determine the sulfotep in technical, the data from Table 8 showed that the amount of sulfotep in technical chlorpyrifos. From these results we found that the sulfotep was 1.103, 7.23, and 0.0456 g/kg of chlorpyrifos content for source I, II, and III respectively. According to [1] the maximum allowed level of sulfotep in technical is 3 g/kg so according to [1] the amount of sulfotep from source III was more than the allowed level and this reflected on the formulation from source III.

This may attributed to the manufacturing process that sulfotep can be produced as by product from hydrolysis of diethyl thionyl phosphoryl chloride (DETC) [79] according to the following equation.



The results obtained from analysis of chlorpyrifos by GC-MS we can easily identify the sulfotep at m/z 322 and Fig. 12 showed that the mass spectrum of sulfotep.

These obtained results were agreement with [57] reported that the sulfotep content of the commercial products didn't show any correlation with storage time.

Also the obtained results were agreement with [51] who found that the sulfotep concentration in diazinon didn't change with time during acid hydrolysis, and also found some of the oldest samples of diazinon formulations had sulfotep concentration lower than some of other formulations analyzed, and this showed that the concentration of sulfotep was not function of the age of the formulation, And also the obtained results were agreement with [3, 62].

1.3. Effect of storage stability on the emulsion stability and re-emulsification for chlorpyrifos 48% EC

The data from Table 9 showed that the emulsion stability and re-emulsification of three commercial chlorpyrifos formulations (manufactured from various companies) after storage at 54 ±2 °C for 1, 3, 7, 14, 21 days. The formulation, when diluted at 30 ±2°C with CIPAC standard waters A and D shall comply with the specifications of chlorpyrifos emulsifiable concentrate. Results indicated that chlorpyrifos from source I, II, and III passed successfully through emulsion stability and re-emulsification test before and after storage at 54 ± °C for 21 days when formulation diluted with CIPAC standard water A.

For source I the emulsion stability and re-emulsification was comply and no precipitate before and after storage at 54 ± 2 °C for 21 days when the formulation diluted with CIPAC standard water D.

But when using CIPAC standard water D in source II and III we found that emulsion stability and re-emulsification before storage in source II has a precipitate layer about 1.0 ml after 0.5 h from dilution and increased after 2 h to 4.5 ml precipitate, also after 24.5 h was 2.2 ml precipitate. The formulation from source II before storage was comply with specifications after 0.5 h, but was not comply after 2 h and 24.5 h. According to [1] the maximum level of cream and precipitate layer don't exceed about 2 ml after 0.5, 2, and 24.5 hrs from dilution. The formulation from source II was comply with specifications at all the periods of storage at 54 ±2 °C after 0.5 h from dilution. Whereas after 2 h from dilution the precipitate was 0.1, 1.7, 0.1, 3.75 and 1.6 ml at 1, 3, 7, 14, and 21 days respectively. Also after 24.5 h from dilution the precipitate was 0, 0.7, 0, 1.8, and 0.6 ml at 1, 3, 7, 14, and 21 days respectively.

For source III the emulsion stability and re-emulsification was comply and no precipitate before storage, but after storage at 54 ±2 °C the emulsion stability after 0.5 h from dilution the precipitate was 0.1, 0.2, 0.3, 0.4, and 0.4 ml at 1, 3, 7, 14, and 21 days respectively, after 2 h from dilution the precipitate was 0.2, 0.25, 0.3, 0.4, and 0.5 ml at 1, 3, 7, 14, and 21 days respectively, and after 24.5 h from dilution no precipitate during the periods of storage. From these obtained results the formulation from source III was comply with the specifications of chlorpyrifos for emulsion stability and re-emulsification after storage at 54 ± 2 °C for 21 days.

The data from Table 10 showed that the emulsion stability and re-emulsification of three commercial chlorpyrifos formulations (manufactured from various companies) after storage at 72 ± 2 °C for 1, 2, 3, 4, 5 days. Results indicated that chlorpyrifos from source I, II, and III passed successfully through emulsion stability and re-emulsification test after storage at 72 ± 2 °C for 5 days when formulation diluted with CIPAC standard water A.

Also when using CIPAC standard water D with chlorpyrifos from source I the emulsion stability and re-emulsification test passed successfully and it was comply with the specification of chlorpyrifos.

But when using CIPAC standard water D with chlorpyrifos from source II, we found that emulsion stability after storage at 72 ±2 °C was as follows after 0.5 h from dilution the precipitate was 0.1, 0.2, 1.0, 0.4, and 3.8 ml at 1, 2, 3, 4, and 5 days respectively, after 2 h from dilution the precipitate was 0.2, 2.0, 3.9, 1.65, and 6.75 ml at 1, 2, 3, 4, and 5 days respectively, after re-emulsification the precipitate after 24.5 h from dilution was 0, 0, 0.2, 0.25, and 0.4 ml at 1, 2, 3, 4, and 5 days respectively.

From these obtained results the emulsion stability after 0.5 h from dilution was comply with the specification at 1, 2, 3 and 4 days after storage at 72 ±2 °C, but it wasn't comply with specification after 5 days, and also it was not comply with the specification after 2 h from dilution at

3, and 5 days, but after re-emulsification, it was comply with specification after 24.5 h from dilution at 1, 2, 3, 4 and 5 days.

However, when using CIPAC standard water D with chlorpyrifos from source III we found that the emulsion stability after storage at 72 ±2 °C was as follows after 0.5 h from dilution the precipitate was 0.1, 0.1, 0.2, 0.3, and 0.5 ml at 1, 2, 3, 4, and 5 days respectively. After 2 h from dilution the precipitate was 0.1, 0.1, 0.3, 0.35, and 0.55 ml at 1, 2, 3, 4, and 5 days respectively.

The re-emulsification passed successfully without any precipitate after 24.5 h from dilution.

From these obtained results the formulation from source III passed successfully through emulsion stability and re-emulsification test after storage at 72 ±2 °C for 5 days, and also it was comply with the specification of chlorpyrifos.

The data from Table 11 showed that the emulsion stability and re-emulsification of three commercial chlorpyrifos formulations (manufactured from various companies) after storage at room temperature for 1, 2, 4, 6, 8, 10, 12 weeks. Results indicated that chlorpyrifos from source I, II, and III passed successfully through emulsion stability and re-emulsification test after storage at room temperature for 12 weeks, when formulation diluted with CIPAC standard water A. also when using CIPAC standard water D in source I and III the emulsion stability and re-emulsification test passed successfully after 10 weeks, and it was comply with the specification of chlorpyrifos. But after 12 weeks appeared a precipitate, and it was 0.2, 2.5, 0.2 ml after 0.5 h, 2 h and 24.5 h respectively from dilution in source I, and also in source III a precipitate was 0.2, 3.9, and 0.2 ml after 0.5 h, 2 h and 24.5 h respectively from dilution.

For source II when using CIPAC standard water D, we found that emulsion stability and re-emulsification was not comply with the specification of chlorpyrifos, where the emulsion stability after 0.5 h from dilution has a precipitate about 1.0, 1.2, 1.9, 2.5, 2.8, 2.9, and 3.0 ml at 1, 2, 4, 6, 8, 10, and 12 weeks respectively.

After 2 h from dilution the precipitate was 4.5, 4.6, 4.7, 4.8, 5, 5.1, and 5.1 ml, at 1, 2, 4, 6, 8, 10 and 12 weeks respectively, and after re-emulsification the precipitate after 24.5 h was 2.5, 2.9, 3.25, 3.6, 3.95, 4.3, and 4.8 ml at 1, 2, 4, 6, 8, 10, 12 weeks respectively.

The previously mentioned results clearly showed that the emulsion stability and re-emulsification of three chlorpyrifos samples was affected by many factors such as manufacturing process and sources of starting materials. The use of various adjuvant and carrier materials in the preparation of the formulation may also result in marked differences in storage stability of formulations. This is especially of concern in the case of generic pesticides, which may be produced and formulated by many manufactures under widely varying conditions, with different materials and under a range of quality control standards.

Also hardness degree of water, variation in temperature degrees and bad storage conditions can be affected on the emulsion stability and re-emulsification. The obtained results were agreement with [45, 48, 64, 65, 67].

1.4. Effect of storage stability on pH values for chlorpyrifos 48% EC.

The data in Table 12 showed that pH values of three commercial chlorpyrifos formulations (manufactured from various companies) after storage at 54 ±2 °C for 1, 3, 7, 14, 21 days. Results indicated that pH values before storage for source I, II, and III were 3.95, 3.95, and 5.55 respectively, and after storage at 54 ±2 °C pH values were 3.95, 4.05, 4.05, 4.04, and 4.1 at 1, 3, 7, 14, and 21 respectively, for source I.

Also for source II pH values were 3.99, 4.06, 3.9, 4.13, and 4.16 at 1, 3, 7, 14, and 21 days respectively. Whereas source III the pH values were 5.89, 6.02, 5.83, 5.87, and 5.62 at 1, 3, 7, 14, and 21 days.

The data in Table 13 showed that pH values of three commercial chlorpyrifos formulations after storage at 72 ± 2 °C for 1, 2, 3, 4, 5 days. Results showed that pH values for source I were 4.1, 4.04, 4.07, 4.06, and 4.05 at 1, 2, 3, 4, and 5 days, and also for source II pH values were 4.13, 3.98, 4.03, 4.10, and 4.15 at 1, 2, 3, 4, and 5 days. While pH values from source III were 5.88, 5.74, 5.46, 5.32, and 5.16 at 1, 2, 3, 4 and 5 days respectively.

The date in Table 14 showed that pH values of three commercial chlorpyrifos formulations after storage at room temperature for 1, 2, 4, 6, 8, 10 and 12 weeks. Results showed that pH values for source I were 3.9, 3.95, 4.04, 4.05, 4, 4.1, and 4.07 at 1, 2, 4, 6, 8, 10 and 12 weeks respectively, and also pH values for source II were 3.99, 3.95, 4.1, 4.05, 4.07, 4.15, and 4.13 at 1, 2, 4, 6, 8, 10 and 12 weeks respectively, but pH values from source III were 5.61, 5.87, 6.02, 5.74, 5.32, 5.83, and 5.75 at 1, 2, 4, 6, 8, 10 and 12 weeks respectively.

From the obtained results we can observe pH range for chlorpyrifos was stable through the periods of storage at elevated temperature.

From [1] reported that pH range for chlorpyrifos between of 4.5 to 6.5. The results from source III were agreement with [1], but the results from source I and II were inagreement with [1].

To find the causes in the variation of pH values from company to other, we measured the free acidity for the technical chlorpyrifos from the three companies, which used in the manufacture process. The free acidity (calculated as H_2SO_4) for technical from source I, II, and III was 1.65, 1.74, and 0.95 g/kg respectively. The maximum level of acidity for technical according to [1] was 1 g/kg, so from the results of acidity for technical we found that acidity was not comply with specification for technical from source I, and II, and it was comply with specification for source III. There was approaching between the two values of acidity for technical from source I and II, and this reflected on the formulation, as there was also approaching between source I and II in pH values. Increasing in acidity of technical for source I and II reflected on pH values for formulation from source I and II.

Table 3. Effect of storage stability on chlorpyrifos 48% EC of three different manufactured sources at 54 ±2 °C.

Storage Periods (Days)	**Source I**		**Source II**		**Source III**	
	Chlorpyrifos content (w/v) %	**Loss %**	**Chlorpyrifos content (w/v) %**	**Loss %**	**Chlorpyrifos content (w/v) %**	**Loss %**
0	47.02 *	0	47.09	0	47.2	0
1	46.95	0.15	46.59	1.06	46.88	0.68
3	46.85	0.36	46.42	1.42	46.6	1.27
7	46.75	0.57	45.67	3.016	46.34	1.82
14	46.1	1.96	45.38	3.63	45.81	2.94
21	45.21	3.85	44.99	4.46	45.43	3.75
t_{95} (days)	27.47 **		23.61		28.19	

* Samples before and after storage stability test analyzed together to reduce the analytical error.

** The time required to reach 95% of the initial chlorpyrifos concentration.

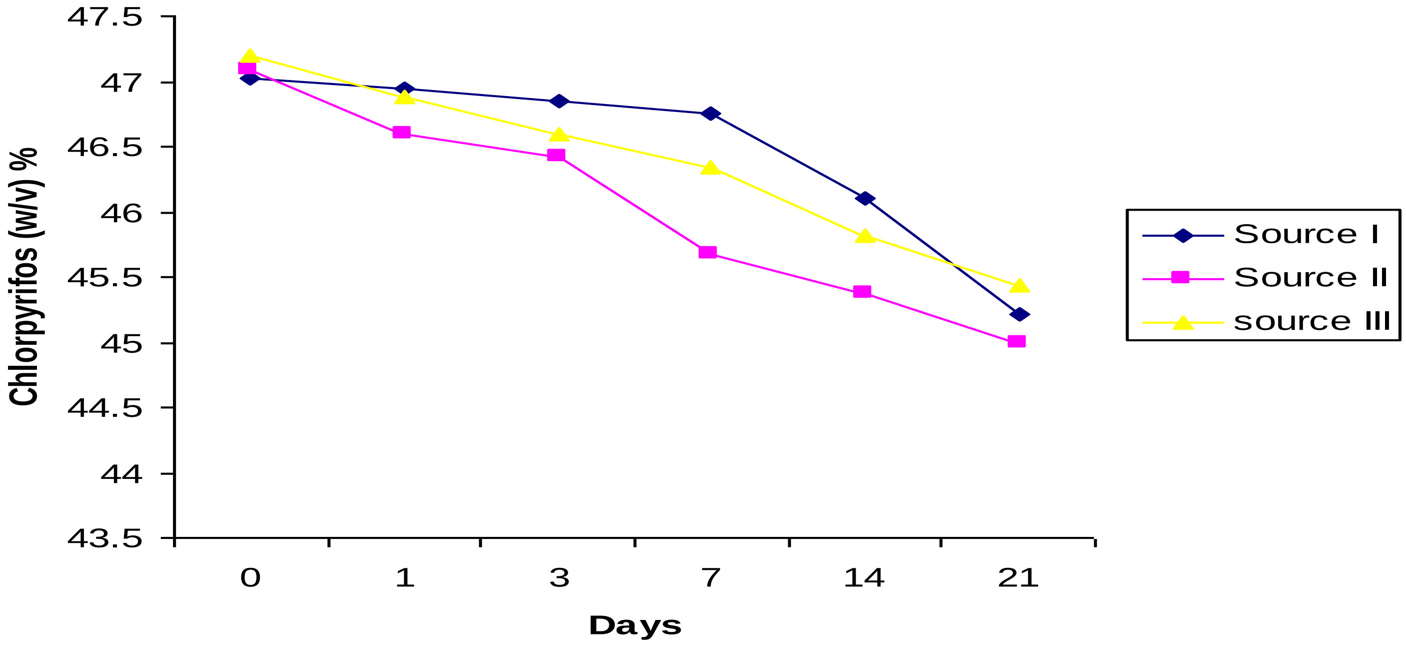


Fig.1. Effect of storage stability on chlorpyrifos 48% EC of three different manufactured sources at 54±2 °C.

Table 4. Effect of storage stability on chlorpyrifos 48 % EC of three different manufactured sources at room temperature.

Storage Periods (Weeks)	**Source I**		**Source II**		**Source III**	
	Chlorpyrifos content (w/v) %	**Loss %**	**Chlorpyrifos content (w/v) %**	**Loss %**	**Chlorpyrifos content (w/v) %**	**Loss %**
0	47.02	0	47.09	0	47.2	0
1	46.87	0.32	46.86	0.49	47.14	0.13
2	46.78	0.51	46.76	0.70	46.77	0.91
4	46.75	0.57	46.47	1.32	46.64	1.19
6	46.68	0.72	46.27	1.74	46.59	1.29
8	46.56	0.98	46.04	2.23	46.46	1.57
10	46.18	1.79	45.93	2.46	46.44	1.61
12	46.025	2.12	45.69	2.97	46.11	2.31
t_{95} (days)	201.46 *		142.78		184.43	

*The time required to reach 95% of the initial chlorpyrifos concentration.

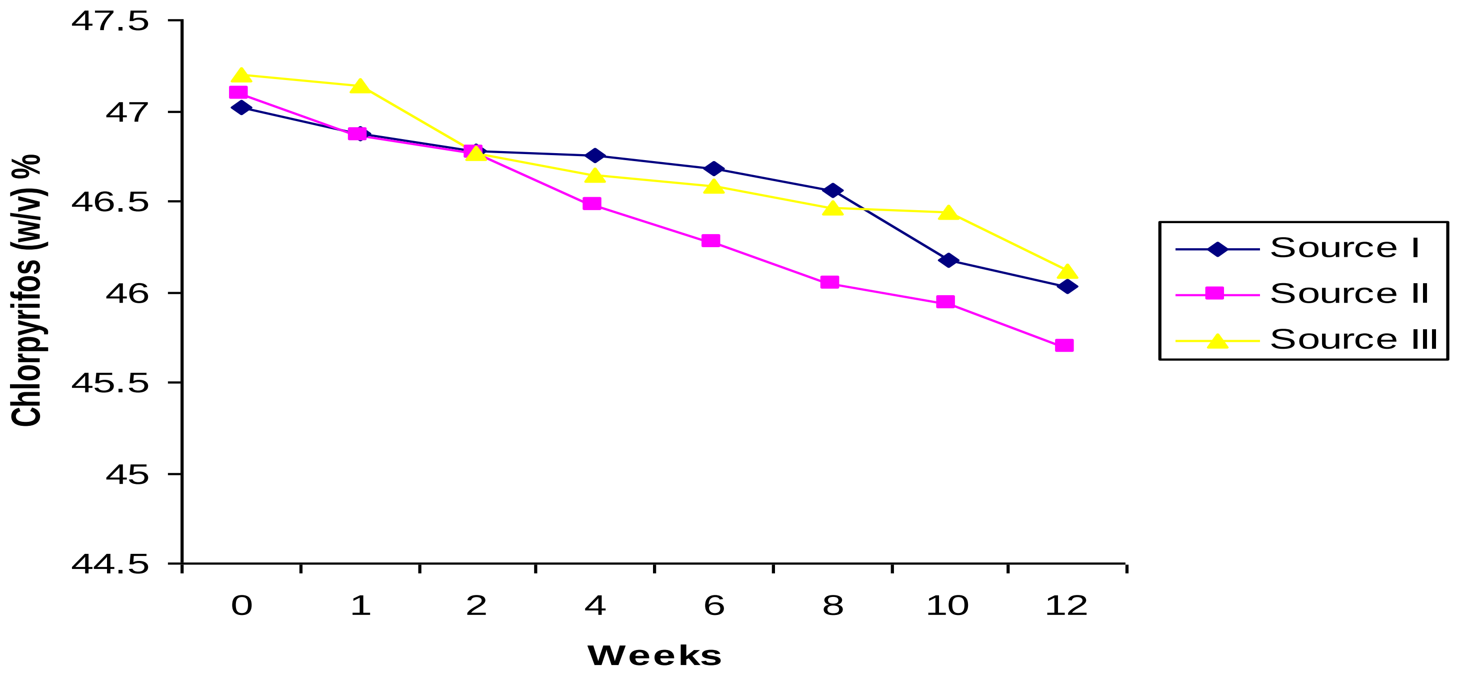


Fig. 2. Effect of storage stability on chlorpyrifos 48 % EC of three different manufactured sources at room temperature.

Table 5. Effect of storage stability on chlorpyrifos 48 % EC of three different manufactured sources at 72 ±2 °C.

Storage Periods (Days)	**Source I**		**Source II**		**Source III**	
	Chlorpyrifos content (w/v) %	**Loss %**	**Chlorpyrifos content (w/v) %**	**Loss %**	**Chlorpyrifos content (w/v) %**	**Loss %**
0	47.02 *	0	47.09	0	47.2	0
1	45.74	2.72	45.22	3.97	45.52	3.56
2	44.69	4.96	44.35	5.82	44.46	5.81
3	44.01	6.4	43.89	6.79	43.52	7.79
4	43.42	7.66	43.74	7.11	42.78	9.36
5	41.79	11.12	41.30	12.30	41.35	12.39
t_{95} (days)	2.18 **		1.95		1.94	

* Samples before and after storage stability test analyzed together to reduce the analytical error.

** The time required to reach 95% of the initial chlorpyrifos concentration.

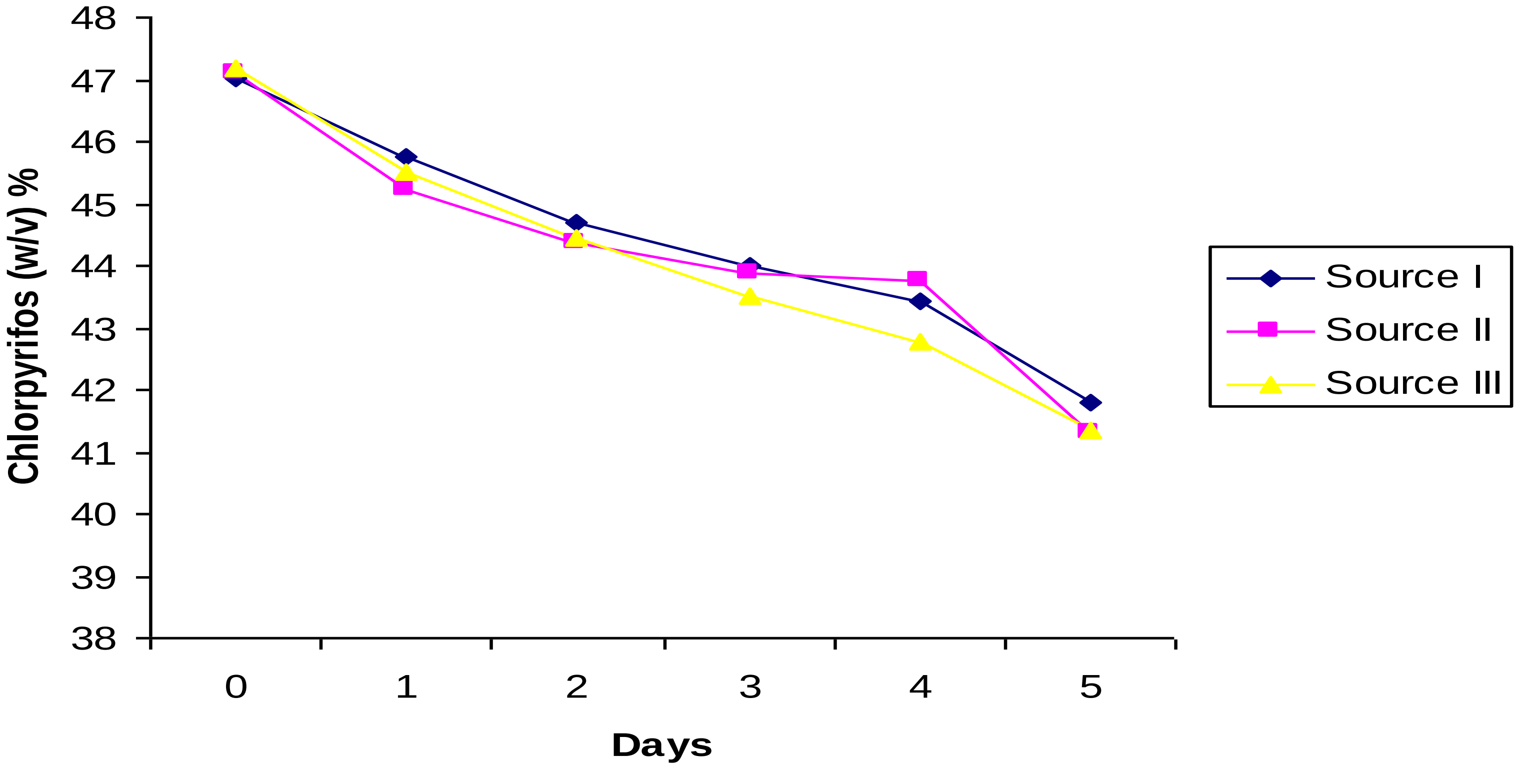


Fig. 3. Effect of storage stability on chlorpyrifos 48 % EC of three different manufactured sources at 72±2 °C.

Table 6. Effect of storage on the amount of sulfotep in chlorpyrifos 48 % EC from three different manufactured sources at 54 ±2 °C, and at 72 ±2 °C.

Storage Periods (Days)	**Source I**				**Source II**				**Source III**			
	Chlorpyrifos content g/kg	Maximum of sulfotep 0.3% of chlorpyrifos found g/kg	Sulfotep found g/kg	Sulfotep as g/kg Of chlorpyrifos	Chlorpyrifos content g/kg	Maximum of sulfotep 0.3% of chlorpyrifos found g/kg	Sulfotep found g/kg	Sulfotep as g/kg Of chlorpyrifos	Chlorpyrifos content g/kg	Maximum of sulfotep 0.3% of chlorpyrifos found g/kg	Sulfotep found g/kg	Sulfotep as g/kg Of chlorpyrifos
0	442.91	1.33	0.55	1.24	441.2	1.32	3.17	7.18	440.27	1.32	0.12	0.27
1	442.25	1.33	0.55	1.24	436.51	1.31	3.22	7.38	437.29	1.31	0.16	0.36
3	441.31	1.32	0.58	1.31	434.92	1.30	3.42	7.86	434.68	1.30	0.15	0.34
7	440.36	1.32	0.57	1.29	427.89	1.28	3.197	7.47	432.25	1.30	0.16	0.37
14	434.24	1.3	0.54	1.24	425.18	1.28	3.29	7.74	427.31	1.28	0.17	0.39
21	425.86	1.28	0.53	1.24	421.52	1.26	3.74	8.87	423.76	1.27	0.14	0.33
At 72 ±2 °C												
0	442.91	1.33	0.55	1.24	441.2	1.32	3.17	7.18	440.27	1.32	0.12	0.27
1	430.85	1.29	0.52	1.21	423.68	1.27	3.16	7.46	424.60	1.27	0.14	0.33
2	420.96	1.26	0.53	1.26	415.53	1.25	3.54	8.52	414.72	1.24	0.1395	0.33
3	414.56	1.24	0.51	1.23	411.22	1.23	3.23	7.85	405.95	1.22	0.1399	0.34
4	408.99	1.23	0.50	1.22	409.81	1.23	3.24	7.91	399.04	1.20	0.13	0.33
5	393.64	1.18	0.46	1.17	391.17	1.17	3.17	8.10	389.72	1.17	0.14	0.36

Table 7. Effect of storage on the amount of sulfotep in chlorpyrifos 48 % EC from three different Manufactured sources at room temperature.

Storage Periods (Weeks)	**Source I**				**Source II**				**Source III**			
	Chlorpyrifos content g/kg	Maximum of sulfotep 0.3% of chlorpyrifos found g/kg	Sulfotep found g/kg	Sulfotep as g/kg Of chlorpyrifos	Chlorpyrifos content g/kg	Maximum of sulfotep 0.3% of chlorpyrifos found g/kg	Sulfotep found g/kg	Sulfotep as g/kg Of chlorpyrifos	Chlorpyrifos content g/kg	Maximum of sulfotep 0.3% of chlorpyrifos found g/kg	Sulfotep found g/kg	Sulfotep as g/kg Of chlorpyrifos
0	442.91	1.33	0.55	1.24	441.2	1.32	3.17	7.18	440.27	1.32	0.12	0.27
1	441.49	1.32	0.55	1.24	439.04	1.32	3.11	7.08	439.71	1.32	0.10	0.23
2	440.65	1.32	0.51	1.16	438.11	1.31	3.14	7.17	436.26	1.31	0.12	0.27
4	440.36	1.32	0.47	1.07	435.39	1.31	3.18	7.30	435.05	1.31	0.12	0.27
6	439.71	1.32	0.56	1.27	433.52	1.30	3.21	7.40	434.58	1.31	0.12	0.27
8	438.58	1.32	0.49	1.12	431.36	1.29	3.14	7.28	433.37	1.30	0.11	0.26
10	434.99	1.30	0.54	1.24	430.33	1.29	3.19	7.41	433.18	1.30	0.12	0.28
12	433.54	1.30	0.51	1.18	428.08	1.28	3.17	7.41	430.11	1.29	0.12	0.27

Table 8. Sulfotep in technical chlorpyrfos

Technical	Chlorpyrifos content g/kg	Sulfotep found g/kg	Sulfotep as g/kg of chlorpyrifos content
I	922.04	1.0172	1.103 *
II	956.32	6.9123	7.23
III	956.35	0.04361	0.0456

* Maximum level of sulfotep in technical = 3 g/kg

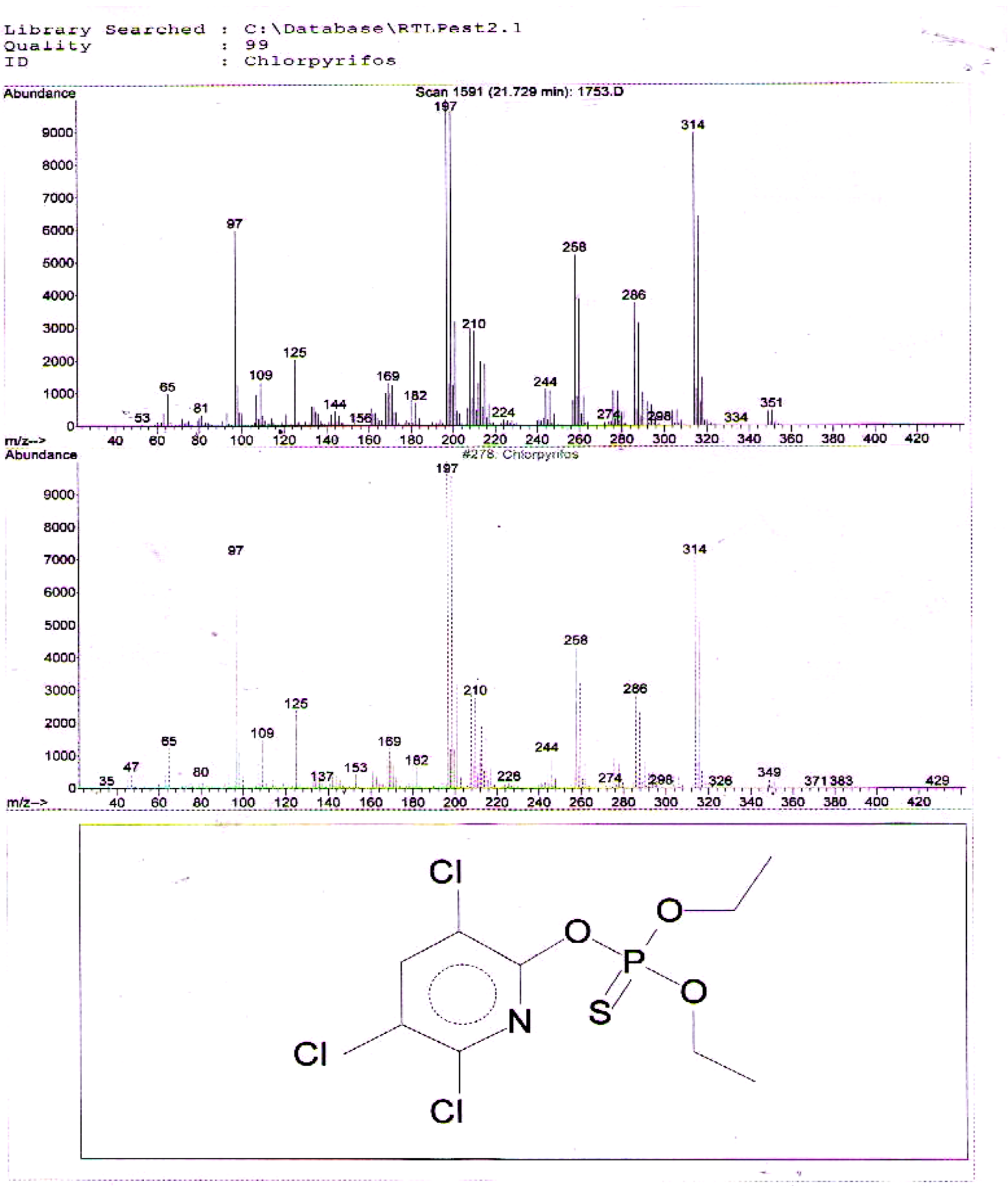


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Fig. 4. Mass spectrum of chlorpyrifos

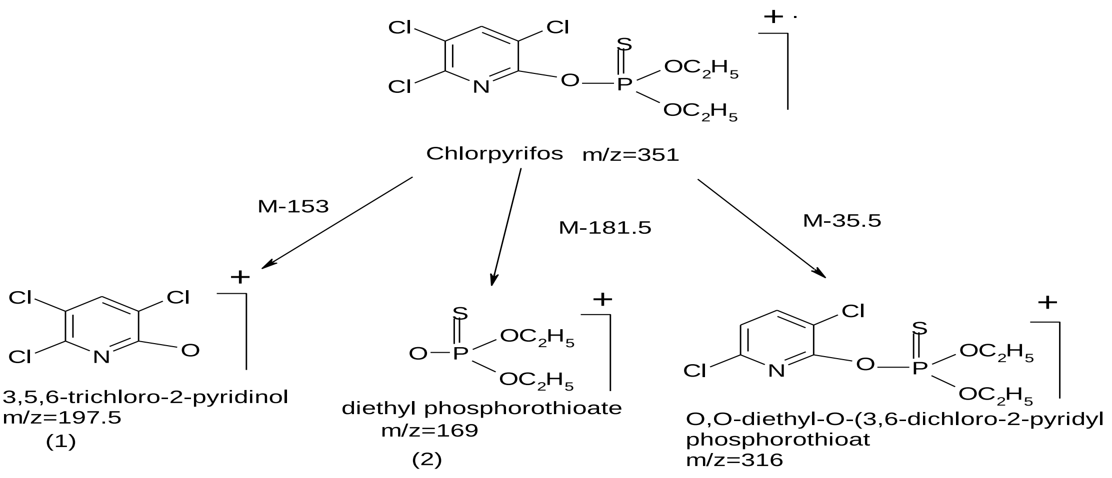


Fig. 5. Possible degradation pathways of chlorpyrifos after storage.

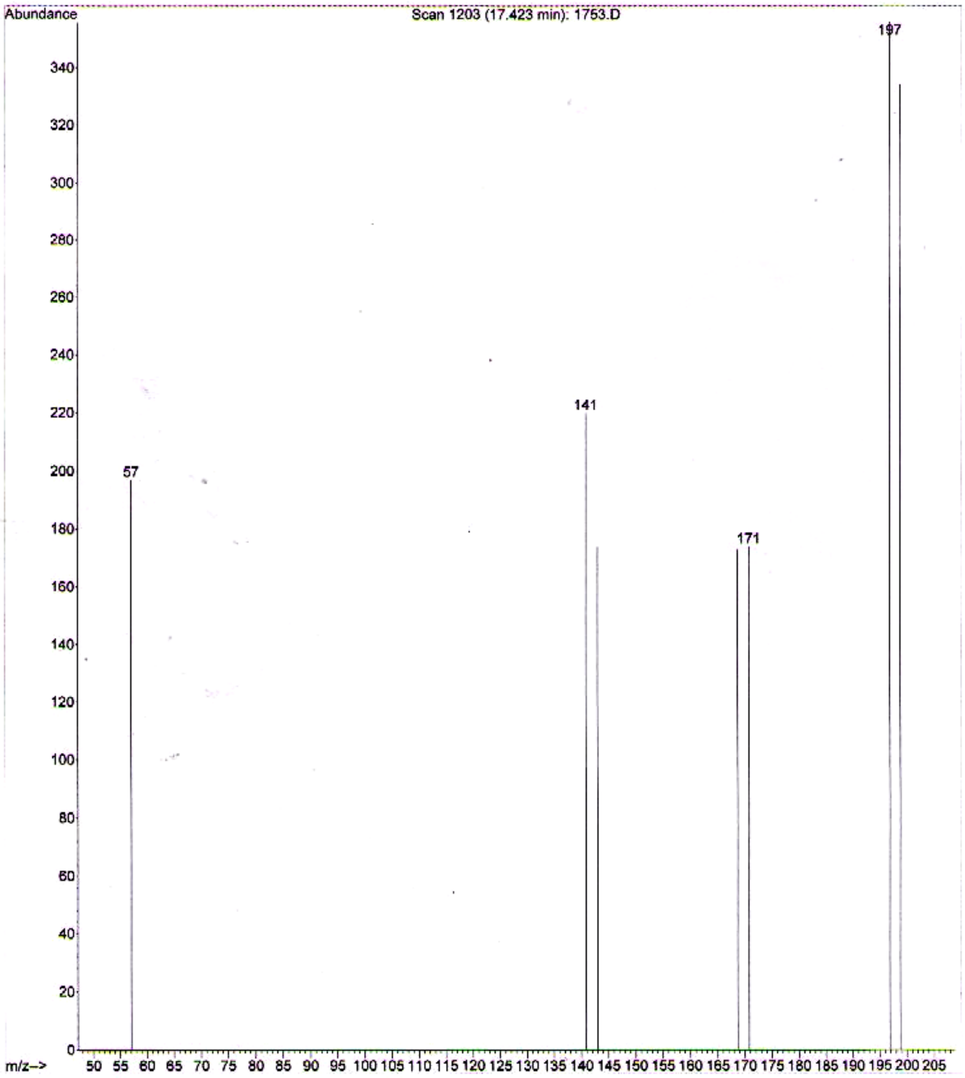
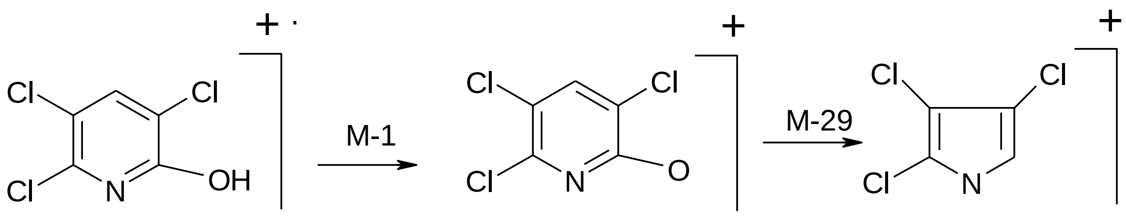


Fig. 6. Mass Spectrum of TCP



3,5,6-trichloro-2-pyridinol (TCP)
m/z=198.5
(1)

m/z=197

m/z=169 [M+1]

Fig. 7. Mass fragmentation of TCP

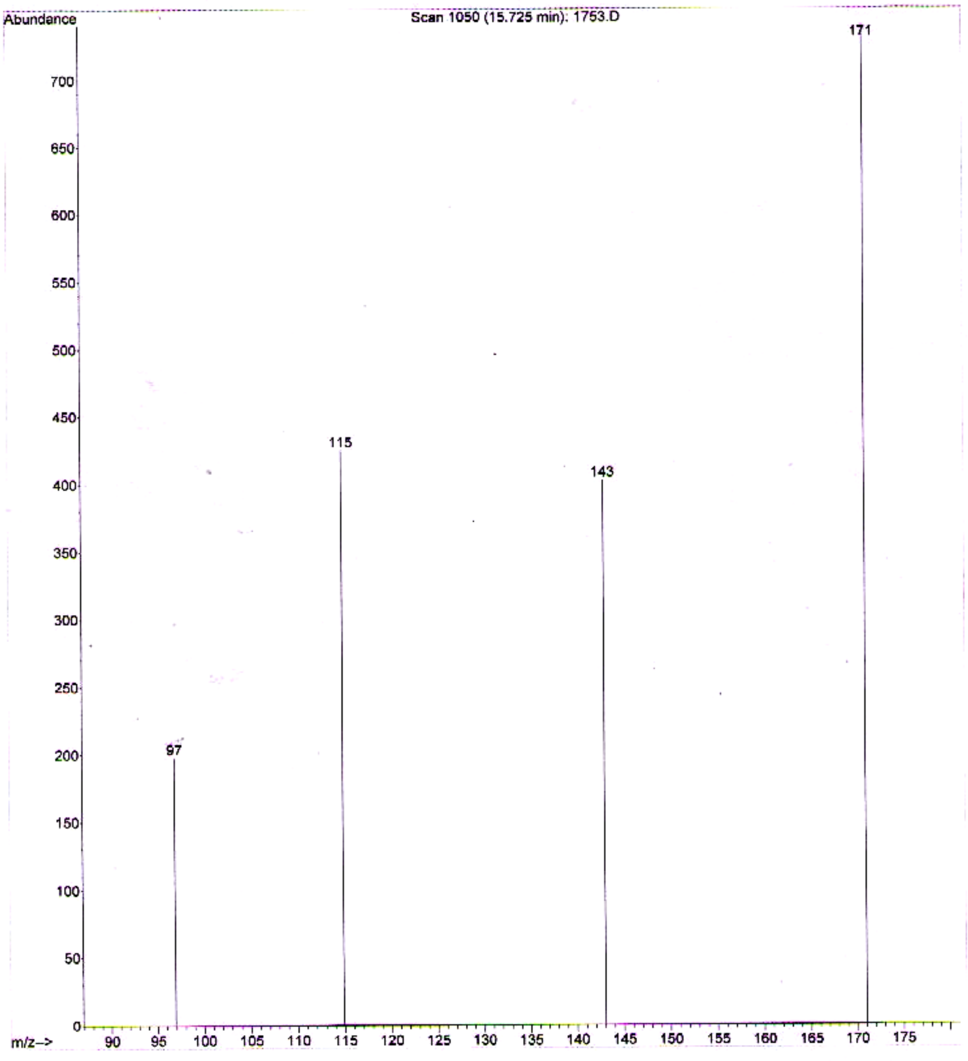
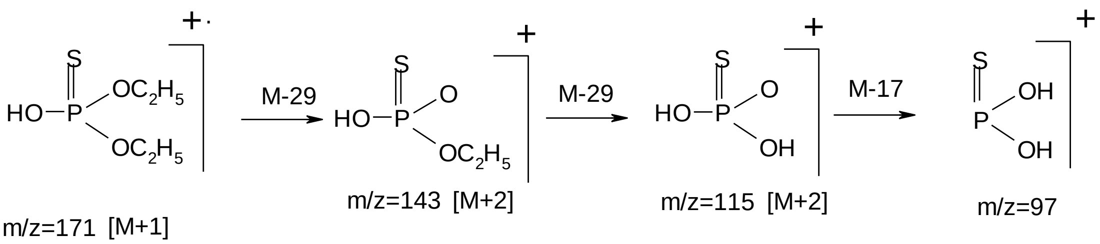


Fig. 8. Mass spectrum of compound no. (2)



(2)

Fig. 9. Mass fragmentation of compound no. (2)

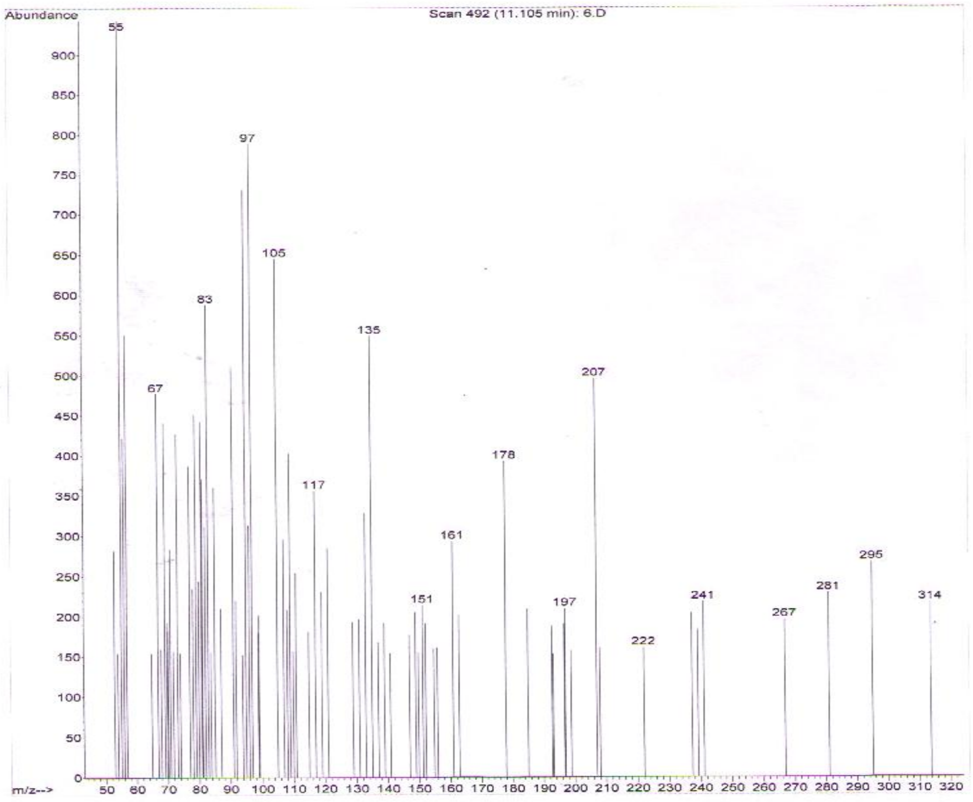


Fig. 10. Mass spectrum of compound no. (3)

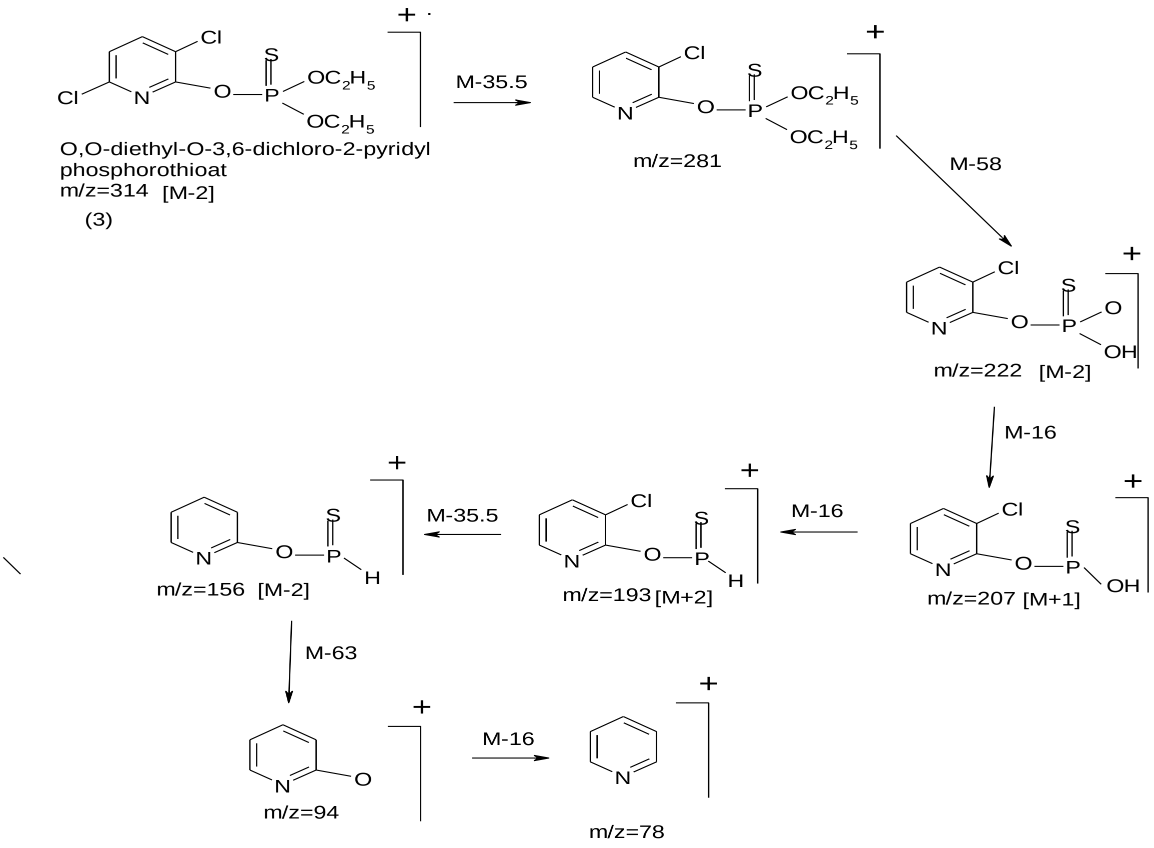
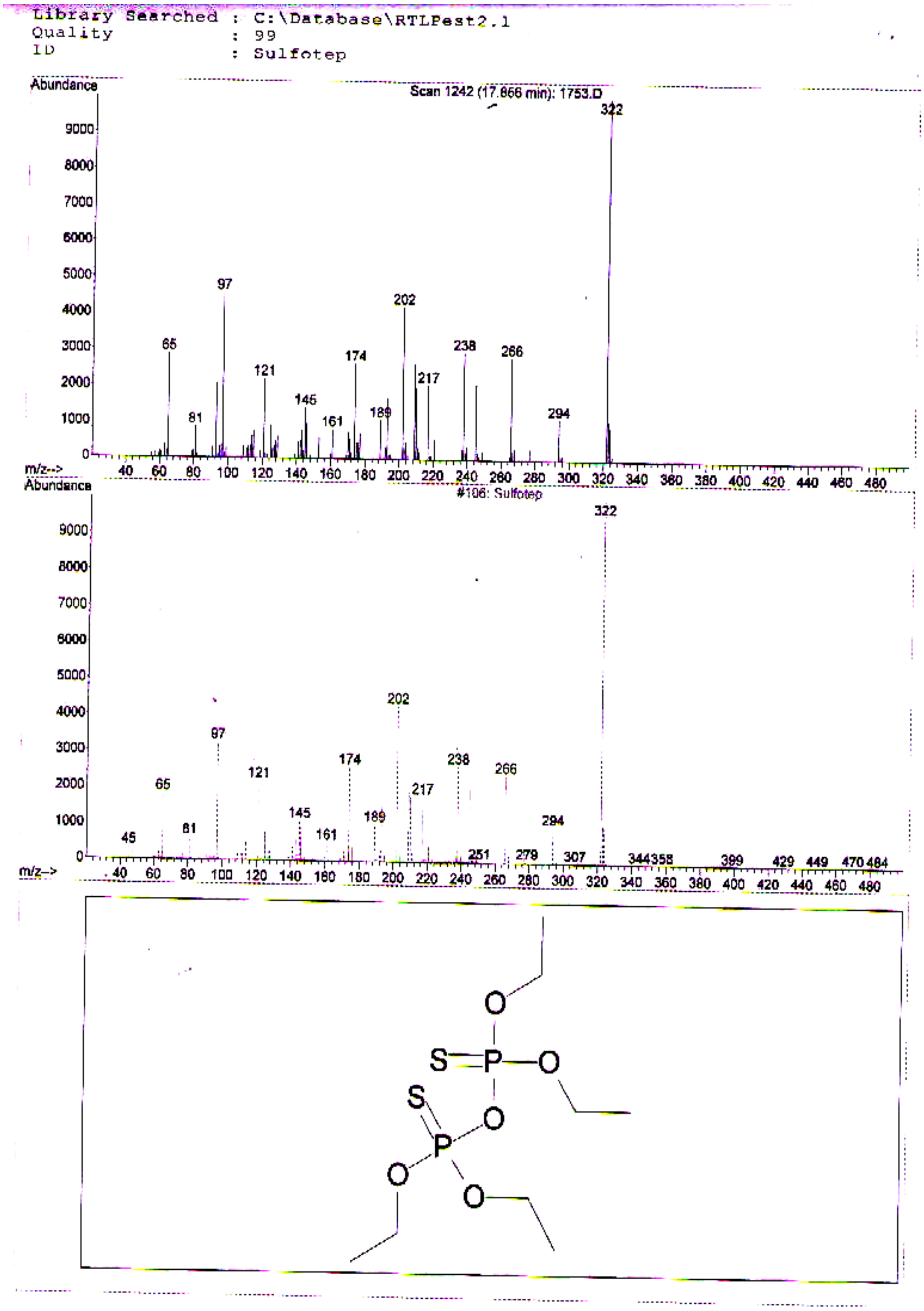


Fig. 11. Mass fragmentation of compound no. (3)



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Library Searched : C:\Database\RTLPest2.1
Quality          : 99
ID               : Sulfotep
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Fig. 12. Mass Spectrum of sulfotep

Table 9. Emulsion stability and re-emulsification for chlorpyrifos 48% EC after storage at 54 ±2 ^{o}C by using CIPAC standard water D.

Storage Periods (Days)	**Source I**			**Source II**			**Source III**		
	0.5 h	2 h	24.5 h	0.5 h	2 h	24.5 h	0.5 h	2 h	24.5h
0	– *	–	–	1 **	4.5	2.2	–	–	–
1	–	–	–	0.1	0.1	–	0.1	0.2	–
3	–	–	–	0.2	1.7	0.7	0.2	0.25	–
7	–	–	–	0.1	0.1	–	0.3	0.3	–
14	–	–	–	0.5	3.75	1.8	0.4	0.4	–
21	–	–	–	0.6	1.6	0.6	0.4	0.5	–

Table 10. Emulsion stability and re-emulsification for chlorpyrifos 48% EC after storage at 72 ±2 ^{o}C by using CIPAC standard water D.

Storage Periods (Days)	**Source I**			**Source II**			**Source III**		
	0.5 h	2 h	24.5 h	0.5 h	2 h	24.5 h	0.5 h	2 h	24.5h
0	– *	–	–	1 **	4.5	2.2	–	–	–
1	–	–	–	0.1	0.2	–	0.1	0.1	–
2	–	–	–	0.2	2	–	0.1	0.1	–
3	–	–	–	1	3.9	0.6	0.2	0.3	–
4	–	–	–	0.4	1.65	0.7	0.3	0.35	–
5	–	–	–	3.8	6.75	1	0.5	0.55	–

* No precipitate

** Volume of precipitate by ml

Table 11. Emulsion stability and re-emulsification for chlorpyrifos 48% EC after storage at room temperature by using CIPAC standard water D.

Storage Periods (weeks)	**Source I**			**Source II**			**Source III**		
	0.5 h	2 h	24.5 h	0.5 h	2 h	24.5 h	0.5 h	2 h	24.5 h
0	– *	–	–	1 **	4.5	2.2	–	–	–
1	–	–	–	1	4.5	2.5	–	–	–
2	–	–	–	1.2	4.6	2.9	–	–	–
4	–	–	–	1.9	4.7	3.25	–	–	–
6	–	–	–	2.5	4.8	3.6	–	–	–
8	–	–	–	2.8	5	3.95	–	–	–
10	–	–	–	2.9	5.1	4.3	–	–	–
12	0.2	2.5	0.2	3	5.1	4.8	0.2	3.9	0.2

** No precipitate

*** Volume of precipitate by ml

Table 12. pH values of chlorpyrifos after storage at 54 ±2 °C

Storage Periods (Days)	**Source I**	**Source II**	**Source III**
0	3.95	3.95	5.55
1	3.95	3.99	5.89
3	4.05	4.06	6.02
7	4.05	3.90	5.83
14	4.04	4.13	5.87
21	4.10	4.16	5.62

Table 13. pH values of chlorpyrifos after storage at 72 ±2 °C

Storage Periods (Days)	**Source I**	**Source II**	**Source III**
0	3.95	3.95	5.55
1	4.10	4.13	5.88
2	4.04	3.98	5.74
3	4.07	4.03	5.46
4	4.06	4.10	5.32
5	4.05	4.15	5.16

Table 14. pH values of chlorpyrifos after storage at room temperature

Storage Periods (Days)	**Source I**	**Source II**	**Source III**
0	3.95	3.95	5.55
1	3.90	3.99	5.61
2	3.95	3.95	5.87
4	4.04	4.10	6.02
6	4.05	4.05	5.74
8	4.00	4.07	5.32
10	4.10	4.15	5.83
12	4.07	4.13	5.75

2. Malathion

2.1. Effect of storage stability on malathion 57% EC content

The data from Table 15 and Fig. 13 showed that the effect of storage at 54 ±2 °C for 1, 3, 7, 14, 21 days on three commercial malathian formulations (manufactured from various companies). Malathion content before storage was 56.53, 56.51, and 56.36% for source I, II, and III respectively.

Results indicated that malathion content after storage for 14 days at 54 ±2 °C was 55.29, 53.53, and 48.17% for source I, II, and III respectively, and it has percentage of loss 2.19, 5.27, and 14.53% for source I, II, III respectively.

Also malathion content after storage for 21 days at 54 ± 2 °C was 55.03, 52.5, and 44.02% for source I, II, and III respectively, and it has percentage of loss 2.65, 7.1, and 21.89% for source I, II, and III respectively. The calculated t_{90} for malathion from source I, II, and III was 82.15, 30.07, and 8.96 days respectively.

According to FAO specifications and evaluations (2004) for malathion mentioned that the content of malathion after storage at 54 ± 2 °C for 14 days shouldn't be lower than 90% relative to the content of malathion before storage and this achieved in malathion from source I, and II, but malathion from source III was not comply to [2] and it has percentage of loss 21.89%.

Whereas malathion was less stable after storage at 72 ± 2 °C, and the data in Table 16 and Fig. 14 showed that malathion content after storage at 72 ± 2 °C for 1, 2, 3, 4 and 5 days.

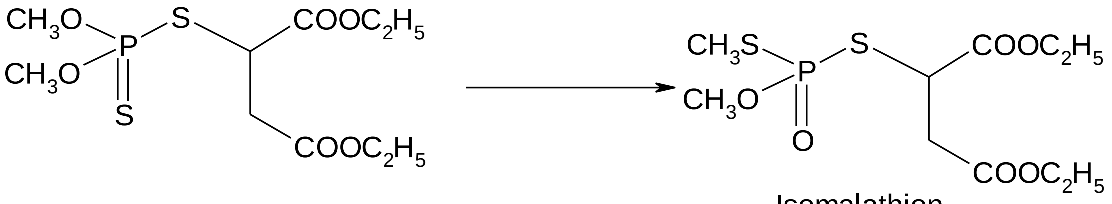
Results indicated that malathion content after storage at 72 ±2 °C for 5 days was 48.49, 47.47, and 38.18% and it has percentage of loss 14.22, 15.99, and 32.26% for source I, II, and III respectively, and also the malathion content from source III was less stable than malathion content from source I and II. The calculated t_{90} for malathion from source I, II, and III was 3.44, 3.02, and 1.35 days respectively.

However malathion was more stable after storage at room temperature for 1, 2, 4, 6, 8, 10, 12 weeks, and Table 17 and Fig. 15 showed that malathion content after storage at room temperature for 12 weeks was 55.59, 54.65, and 52.33% and it has percentage of loss 1.67, 3.45, and 7.15% for source I, II, and III respectively. The calculated t_{90} for malathion from source I, II, and III was 528, 252.12, and 119.34 days respectively.

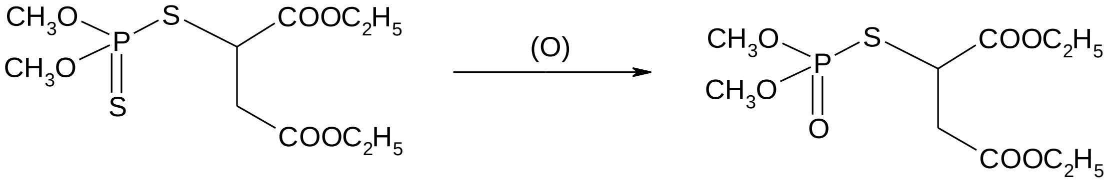
According to the tolerances (± 2.5%) for malathion in [2], the malathion from source I was comply with specification after storage at room temperature for 12 weeks, but for source II the malathion content was not comply with specification after 4 weeks from storage at room temperature. Whereas malathion from source III was less stable and was not comply with specification after 2 weeks from storage at room temperature.

The previously mentioned results clearly showed that there is a difference in the rate of degradation of the three malathion formulations under investigation because of many factors like change in temperature degrees and long period of storage, but also there are another important factors such as manufacturing process and sources of starting materials. The use of various surfactants and carrier materials in the preparation of formulation may also result in marked differences in storage stability of formulations.

Organophosphates are normally stable at ambient temperatures, but at elevated temperatures, good yields of isomers may be obtained. In case of malathion the P = S (thiono) linkage may isomerizes to the P-S-(thiolo) form and the product may be substantially more toxic to mammals. The toxicity of malathion to human is quite low, but the presence of more than 2% of isomalathion, the s-methyl isomer, in manufactured product used for malaria control led to an outbreak of poisoning among 7500 workers [80].

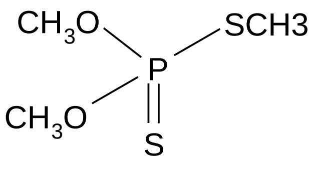

Malathion Isomalathion

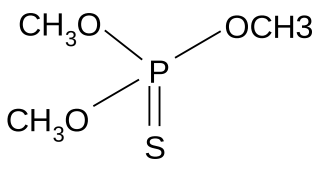
In the environment, the thiophosphoryl bond (P=S) of malathion can be oxidized to their corresponding (P=O) oxon by various oxidizing agents such as ozone, dinitrogen tetroxide, peracid and chlorine [81, 82, 83, 84, 85]. In the atmosphere, gas-phase malathion can be oxidized to malaoxon by atmospheric oxidants such as ozone, nitrate, radicals and OH radicals [58].



Malathion Malaoxon

Also malathion can be degraded to two impurities MeOOSPS-triester and MeOOOPS-triester, and can be identified and quantified by GC-FID, we will explain this part in details in the part of impurities of malathion.


MeOOSPS-triester


MeOOOPS-triester

The presented results of malthion after storage were in line with [17, 33, 45].

2.2. Effect of storage on the formation of malathion impurities

2.2.1. Impurities of malathion from source I

The data presented in Tables (18, 19) showed that the effect of storage on the amount of Malathion impurities at 54 ±2 °C for 1, 3, 7, 14, 21 days. The amount of isomalathion, malaoxon, MeOOSPS–triester, and MeOOOPS–triester in malathion formulation before storage was 23.57, 11.09, 4.60, and 2.89 g/kg respectively.

For isomalathion content in malathion formulation after storage at 54 ±2 °C for 14, and 21 days was 27.96, and 30.16 g/kg respectively, where the maximum level of isomalathion in malathion emulsifiable concentrate is 0.8% of malathion content as from the obtained results the maximum level was 4.15 and 4.13 g/kg at 14, and 21 days respectively. From these obtained results the amount of isomalathion was more than the maximum allowed limit for isomalathion in malathion formulation before and after storage at 54 ±2 °C.

For malaoxon content in malathion formulation after storage at 54 ±2 °C for 14, and 21 days was 16.97, and 17.16 g/kg respectively, where the maximum level of malaoxon in malathion emulsifiable concentrate is 0.1% of malathion content as from the obtained results the maximum level was 0.518 and 0.516 g/kg at 14, and 21 days respectively. From these results the amount of malaoxon was more than the maximum allowed limit for malaoxon in malathion formulation before and after storage at 54 ±2 °C.

For MeOOSPS–triester content in malathion formulation after storage at 54 ±2 °C for 14, and 21 days was 5.28, and 5.40 g/kg respectively, where the maximum level of MeOOSPS–triester in malathion emulsifiable concentrate is 1.6 % of malathion content as from the obtained results the maximum level was 8.29, and 8.26 g/kg at 14, and 21 days respectively. From these results amount of MeOOSPS–triester was less than the maximum allowed limit for MeOOSPS–triester in malathion formulation before and after storage at 54 ±2 °C.

For MeOOOPS–triester in malathion formulation after storage at 54 ±2 °C for 14, and 21 days was 5.65, and 5.71 g/kg respectively, where the maximum level of MeOOOPS–triester in malathion emulsifiable concentrate is 0.5% of malathion content as from the obtained results the maximum level was 2.59, and 2.58 g/kg at 14, and 21 days respectively. From these results the amount of MeOOOPS–triester was more than the maximum allowed limit for MeOOOPS–triester in malathion formulation before and after storage at 54 ±2 °C.

The data from Tables (20, 21) showed that the effect of storage on the amount of malathion impurities at 72 ±2 °C for 1, 2, 3, 4, 5 days.

For isomalathion, malaoxon, MeOOSPS–triester, and MeOOOPS–triester content in malathion formulation after storage at 72 ±2 °C for 5 days was 59.25, 19.76, 6.11, and 8.02 g/kg respectively. For all impurities of malathion were more than the maximum level of impurities except the MeOOSPS–triester, where the maximum level for it was 7.28 g/kg.

The data from Tables (22, 23) showed that the effect of storage on the amount of malathion impurities at room temperature for 12 weeks.

For the content of isomalathion, malaoxon, MeOOSPS–triester, and MeOOOPS–triester in malathion formulation after storage at room temperature for 12 weeks was 43.82, 22.61, 5.18 and 7.23 g/kg respectively. For all impurities of malathion were more than the maximum level of impurities except the MeOOSPS–trimester, the maximum level for it was 8.34 g/kg.

2.2.2. Impurities of malathion from source II

The data from Tables (24, 25) showed the effect of storage on the amount of malathion impurities at 54 ±2 °C for 1, 3, 7, 14, 21 days.

The amount of isomalathion, malaoxon, MeOOSPS–triester, and MeOOOPS–triester is malathion formulation before storage was 18.95, 36.68, 5.57, and 2.24 g/kg respectively.

For isomalathion content in malathion formulation after storage at 54 ±2 °C for 14, and 21 days was 31.71, and 35.55 g/kg respectively, where the maximum level was 3.96, and 3.88 g/kg at 14, and 21 days respectively. From these obtained results the amount of isomalathion was more than the maximum allowed limit for isomalathion in malathion formulation.

For malaoxon content in malathion formulation after storage at 54 ±2 °C for 14, and 21 days was 62.63, and 64.29 g/kg respectively, where the maximum allowed level was 0.495, and 0.485 g/kg at 14, and 21 days respectively. From these obtained results the amount of malaoxon was more than the maximum allowed limit for malaoxon in malation formulation.

For MeOOSPS–triester content in malathion formulation after storage at 54 ±2 °C for 14 and 21 days was 6.79, and 9.05 g/kg respectively, where the maximum allowed level was 7.92, and 7.76 g/kg at 14, and 21 days. From these obtained results the amount of MeOOSPS–triester was less than the maximum allowed limit after 14 days, and more than the maximum allowed limit after 21 days.

For MeOOOPS–triester content in malathion formulation after storage at 54 ±2 °C for 14 and 21 days was 4.41, and 5.21 g/kg respectively, where the maximum allowed level was 2.47, and 2.43 g/kg at 14, and 21 days respectively. From these obtained results the amount of MeOOOPS–triester was more than the maximum allowed limit for MeOOOPS–triester in malathion formulation.

The data from Tables (26, 27) showed that the effect of storage on the amount of malathion impurities at 72 ±2 °C for 1, 2, 3, 4, 5 days. For isomalathion, malaoxon, MeOOSPS–triester, and MeOOOPS–triester content in malathion formulation after storage at 72 ±2 °C for 5 days was 30.81, 67.80, 8.66, and 7.54 g/kg respectively, where the maximum allowed level was 3.51, 0.44, 7.02, and 2.19 g/kg respectively. From these obtained results all impurities of malathion were more than the maximum allowed level of impurities in malathion formulation.

The data from Tables (28, 29) showed that the effect of storage on the amount of malathion impurities at room temperature for 12 weeks. For the content of isomalathion, malaoxon, MeOOSPS–triester, and MeOOOPS–triester in malathion formulation after storage at room temperature for 12 weeks was 28.24, 57.70, 8.27, and 8.69 g/kg respectively. For all impurities of malathion were more than the maximum level of impurities in malathion formulation.

2.2.3. Impurities of malathion from source III

The data from Tables (30, 31) showed that the effect of storage on the amount of malathion impurities at 54 ±2 °C for 1, 3, 7, 14, 21 days. The amount of isomalathion, malaoxon, MeOOSPS–triester, and MeOOOPS–triester in malathion formulation before storage was 156.27, 8.17, 21.45, and 4.06 g/kg respectively, and all impurities of malathion were more than the maximum level of impurities in malathion formulation.

For isomalathion content in malathion formulation after storage at 54 ±2 °C for 14, and 21 days was 198.12, and 218.24 g/kg respectively, for malaoxon content was 13.43, and 17.08 g/kg at 14, and 21 days respectively. Also MeOOSPS–triester content was 30.35, and 33.55 g/kg at 14, and 21 days respetively, and for MeOOOPS–triester content was 7.80 and 9 g/kg at 14, and 21 days respectively. From the obtained results all impurities of malathion were more the maximum allowed level of impurities in malathion formulation after storage at 54 ±2 °C for 21 days.

The data from Tables (32, 33) showed that the effect of storage on the amount of malathion impurities at 72 ±2 °C for 5 days. For isomalathion, malaoxon, MeOOSPS–triester, and MeOOOPS–triester content in malathion formulation after storage at 72 ±2 °C for 5 days was 273.42, 24.34, 41.95, and 15.55 g/kg respectively. From these obtained results all impurities of malathion were more than the maximum allowed level of impurities in malathion formulation.

The data from Tables (34, 35) showed that the effect of storage on the amount of malathion impurities at room temperature for 12 weeks. For the content of isomalathion, malaoxon, MeOOSPS–triester, and MeOOOPS–triester in malathion formulation after storage at room temperature for 12 weeks was 191.89, 12.40, 29.70, and 8.50 g/kg respectively. For all impurities of malathion were more than the maximum level of impurities in malathion formulation.

The previously mentioned results clearly showed that the amount of impurities in malathion formulation from three sources was affected by many factors such as manufacturing process and sources of starting materials. The used of various adjuvants and carrier materials in the preparation of the formulation may also result in marked differences in storage stability of formulations.

Also variation in temperature degrees can be affected on increasing of impurities in malathion, and the presence of impurities in technical malathion can be also affected on presence of the impurities in malathion formulation. By the analysis of technical malathion from three sources (manufactured from various companies) to identify and determine the impurities in technical, the data from Table 36 showed that the amount of impurities in technical malathion. From these results we found that the isomalathion was 19.08, 35.06, and 23.57 g/kg, malaoxon was 1.74, 1.35, and 1.40 g/kg, MeOOSPS–triester was 6.02, 4.20, and 3.52 g/kg, and MeOOOPS–triester was 0.106, 1.40, and 0.47 g/kg for source I, II, and III respectively.

The P = S (thiono) linkage in malathion can be isomerize to the P-S (thiolo) form to form isomalathion, and this product is more toxic than malathion.

Also there is another transformation in malathion by oxidation to form malaoxon.

From the previously mentioned results we found the amount of all impurities in malathion increased by storage at 54 ±2 °C, 72 ±2 °C, and room temperature. These results were in line with [50] reported that storage of technical malathion for 3 to 6 months at 40°C resulted in materials which more toxic such as isomalathion and malaoxon. Also the obtained results were in line with [2] mentioned that isomalathion increased by storage and storage produced small amounts of MeOOSPS–triester, and MeOOOPS–triester.

2.3. Effect of storage stability on the emulsion stability and re-emulsification for malathion 57% EC

The data from Table 37 showed that the emulsion stability and re-emulsification of three commercial malathion formulations (manufactured from various companies) after storage at 54 ±2 °C for 1, 3, 7, 14, 21 days. The formulation when diluted at 30 ±2 °C with CIPAC standard waters A and D shall comply with the specifications of malathion emulsiable concentrate.

Results indicated that malathion from source I, II, and III passed successfully through the emulsion stability and re-emulsification test before and after storage at 54 ±2 °C for 21 days when formulation diluted with CIPAC standard water A.

For malathion from source I the emulsion stability and re-emulsification was comply and no precipitate before and after storage at 54 ±2 °C for 21 days when the formulation diluted with CIPAC standard water D.

But when using CIPAC standard water D with malathion from source II we found that emulsion stability and re-emulsification before storage has a precipitate layer about 3.75 ml after 0.5 h from dilution and increased after 2 h to 8.8 ml precipitate.

Also there was a precipitate about 6.8 ml after re-emulsification 24.5 h. According to [2] the maximum level of cream or precipitate layer doesn't exceed about 2 ml after 0.5h and 4 ml after 2h, 24.5h from dilution with CIPAC standards water A and D. The formulation from source II was not comply with specifications before storage, but after storage at 54 ±2 °C the precipitate layer increased after 1 day from storage and decreased until the precipitate layer became about 1.5 ml after 0.5h for dilution at 21 days, and after 2 h the precipitate was 4.8 ml, at last after 24.5 h from dilution there was not any precipitate. From these results the formulation from source II was not comply with specifications after storage at 54 ±2 °C but we found that the precipitate decreased during and after storage at 54 ±2 °C for 21 days.

For source III the emulsion stability and re-emulsification was not comply with specifications before storage, where there was a precipitate about 3.5 ml after 0.5h from dilution, and increased to 6.6 ml after 2 h from dilution, and decreased to 3.5 ml after 24.5 h from dilution with CIPAC standard water D.

After storage at 54 ±2 °C emulsion stability after 0.5 h from dilution the precipitate was 1.90, 2.70, 0.60, and 0 ml at 1, 3, 7, 14, and 21 days respectively, after 2 h from dilution the precipitate was 6.60, 5.70, 7.30, 4.50, 1.25, and 0 ml at 1, 3, 7, 14, and 21 days respectively, and after 24.5 h from dilution there wasn't any precipitate at 1, 3, 7, 14, and 21 days.

The data from Table 38 showed that the emulsion stability and re-emulsification of three commercial malathion formulations (manufactured from various companies) after storage at 72 ±2 °C for 1, 2, 3, 4, 5 days. Results indicated that malathion from source I, II, and III passed successfully through the emulsion stability and re-emulsification test after storage at 72 ±2 °C for 5 days when formulation diluted with CIPAC standard water A. Also when using CIPAC standard water D with malathion from source I the emulsion stability and re-emulsification test passes successfully and it was comply with the specification of malathion.

But when using CIPAC standard water D with malathion from source II, we found that emulsion stability after storage at 72 ±2 °C was as follow, after 0.5 from dilution the precipitate was 5.50, 4.60, 3.30, 1.80, and 0.70 ml at 1, 2, 3, 4, and 5 days respectively, after 2 h from dilution the precipitate was 8.70, 7.80, 6.45, 5.50, and 3.60 ml at 1, 2, 3, 4, and 5 days respectively, and after re-emulsification the precipitate after 24.5h from dilution was 6, 4.70, 1.20, 0.60, and 0 ml at 1, 2, 3, 4, and 5 days respectively. From these obtained results the emulsion stability and re-emulsification wasn't comply with specification at 1, 2, and 3 days, but after 4, and 5 days was comply with specification after 0.5 h from dilution.

However, when using CIPAC standard water D with the malathion from source III we found that the emulsion stability after storage at 72 ±2 °C was as follows, after 0.5 h from dilution the precipitate was 4.30, and 1.95 ml at 1, and 2 days, and then there wasn't any precipitate after 3, 4, and 5 days from storage at 72 ±2 °C.

After 2 h from dilution the precipitate was 6.70, and 5.80 ml at 1, and 2 days and the precipitate disappeared at 3, 4, and 5 days, and also there was not any precipitate after re-emulsification after 24.5h from dilution at 1, 2, 3, 4, and 5 days.

From these obtained results the formulation from source III wasn't comply with specification after 1 day from storage at 72 ±2 °C, but after 2, 3, 4, and 5 days was comply with specification, and the formulation passed successfully through emulsion stability and re-emulsification.

The data from Table 39 showed that the emulsion stability and re-emulsification of three commercial malathion formulations (manufactured from various companies) after storage at room temperature for 1, 2, 4, 6, 8, 10, 12 weeks. Results indicated that malathion from source I, II, and III passed successfully through emulsion stability and re-emulsification test after storage at room temperature for 12 weeks when formulation diluted with CIPAC standard water A. Also when using CIPAC standard water D with malathion from source I the emulsion stability and re-emulsification test passed successfully after 12 weeks, but after 12 weeks, but there was a precipitate about 1.10, 4, and 0.2 ml after 0.5, 2, and 24.5 h respectively from dilution.

For malathion from source II when using CIPAC standard Water D, we found that the emulsion stability and re-emulsification was not comply with specification of malathion, as there was increasing in the precipitate wit increasing the period of storage until 12 weeks the precipitate was 5.70, 9.10, and 9 ml after 0.5, 2, and 24.5 h respectively from dilution.

Also for malathion from source III when using CIPAC standard water D, we found that the emulsion stability and re-emulsification was not comply with specification of malathion, as there was increasing in the precipitate with increasing the period of storage until 12 weeks the precipitate was 6.20, 8, and 8.50 ml after 0.5, 2, and 24.5 h respectively from dilution.

The previously mentioned results clearly showed that the emulsion stability and re-emulsification of three malathion samples was affected by storage at elevated temperature, and we found decreasing in the precipitate with long period of storage, but at room temperature there was increasing in the precipitate with long period of storage, this evidence on the formulations from source II, and III were so bad because of many factors such as manufacturing process and sources of starting materials. The use of various adjuvants and carrier materials in the preparation of the formulation may also result in marked differences in storage stability of formulations. This is especially of concern in the case of generic pesticides, which may be produced and formulated by many manufactures under widely varying conditions, with different materials. The obtained results were agreement with [45, 48, 64, 65, 67].

2.4. Effect of storage stability on acidity for malathion 57% EC

The data from Table 40 and Fig. 16 showed that free acidity calculated as H_2SO_4 of three commercial malathion formulations (manufactured from various companies) after storage at 54 ±2 °C for 1, 3, 7, 14, 21 days. Results indicated that free acidity before storage for source I, II, and III was 1.67, 5.11, and 6.83 g/kg calculated as H_2SO_4 respectively.

After storage at 54 ±2 °C for 14 days free acidity was 3.19, 6.55, and 8.13 for source I, II, and III respectively and it increased after 21 days to 4.03, 7.01, and 8.49 g/kg for source I, II, and III.

The data from Table 41 and Fig. 17 showed that free acidity calculated as H_2SO_4 of three commercial malathion formulation after storage at 72 ±2 °C for 5 days. Results showed that there was increasing in acidity with increasing in time and temperature, and we found that free acidity calculated as H_2SO_4 after storage at 72 ±2 °C for 5 days was 4.63, 7.22, and 9.94 g/kg for source I, II, and III respectively.

The data from Table 42 and Fig. 18 showed that free acidity calculated as H_2SO_4 of three commercial malathion formulations after storage at room temperature for 12 weeks. Results indicated that also there was increasing in acidity with increasing in time, and we found that free acidity calculated as H_2SO_4 after storage at room temperature for 12 weeks was 3.62, 9.38, and 10.46 g/kg for source I, II, and III respectively.

According to [2] reported that the maximum level of acidity before storage 2 g/kg calculated as H_2SO_4 and 3 g/kg after storage at 54 ±2 °C for 14 days. From the obtained results we can observe increasing in acidity with increasing in time and temperature, and according to [2] acidity of malathion from source II, and III was not comply with specification before and after storage at room temperature, 54 and 72 ±2 °C, but acidity of malathion from source I was comply before and after storage at 54 ±2 °C for 14 days, but after 21 days was not comply with specification, and also it wasn't comply with specification after storage at 72 ±2 °C and room temperature.

To find the causes in the variation of acidity from company to other, we measured the free acidity for the technical malathion from the three companies, which used in the manufacture process. The free acidity for technical from source I, II, and III was 1.1, 2.5 and 3.5 g/kg (calculated as H_2SO_4) respectively. According to [2] the maximum level of acidity for technical is 2 g/kg from the result of acidity for technical, we found that acidity was comply with specification for source I, and not comply with specification for source II, and III, and this reflected on the formulation from source I, II, and III.

Some pesticides increase in acidity during storage and this makes them more likely to corrode containers from within.

According to [86] reported that the experimental results clearly showed that acidity limits are suitable quality criteria for active ingredients that form acidic decomposition products, and for their emulsifiable concentrates.

Table 15. Effect of storage stability on malathion 57% EC of three different manufactured sources at 54 ±2 °C

Storage Periods (Days)	**Source I**		**Source II**		**Source III**	
	Malathion content (w/v) %	**Loss %**	**Malathion content (w/v) %**	**Loss %**	**Malathion content (w/v) %**	**Loss %**
0	56.53 *	0	56.51	0	56.36	0
1	56.32	0.37	55.38	1.99	54.00	4.19
3	55.83	1.24	55.26	2.21	52.90	6.14
7	55.52	1.78	55.11	2.48	50.8	9.87
14	55.29	2.19	53.53	5.27	48.17	14.53
21	55.03	2.65	52.50	7.1	44.02	21.89
t_{90} (days)	82.15 **		30.07		8.96	

* Samples before and after storage stability test analyzed together to reduce the analytical error.

** The time required to reach 90% of the initial malathion concentration.

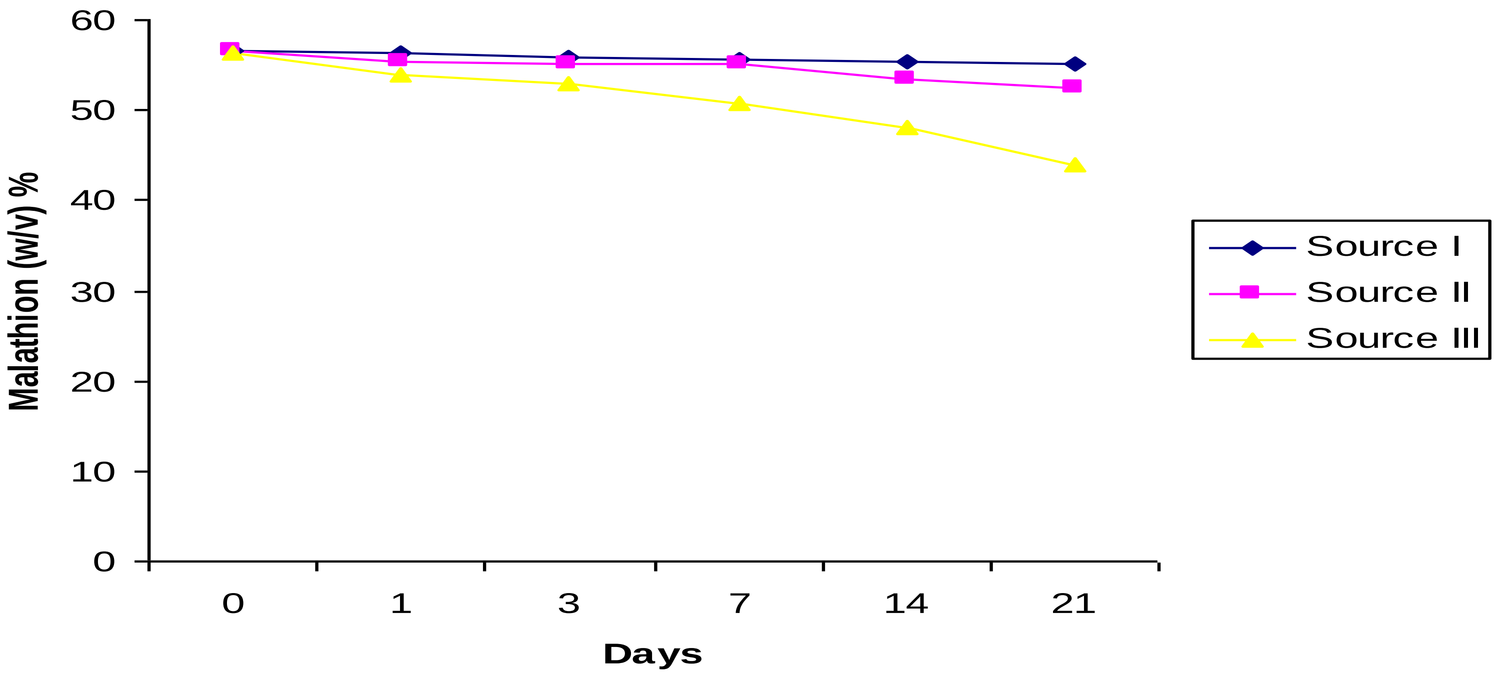


Fig. 13. Effect of storage stability on malathion 57% EC of three different manufactured sources at 54 ±2 °C.

Table 16. Effect of storage stability on malathion 57% EC of three different manufactured sources at 72 ±2 °C

Storage Periods (Days)	**Source I**		**Source II**		**Source III**	
	Malathion content (w/v) %	**Loss %**	**Malathion content (w/v) %**	**Loss %**	**Malathion content (w/v) %**	**Loss %**
0	56.53 *	0	56.51	0	56.36	0
1	55.17	2.41	54.46	3.63	50.88	9.72
2	53.92	4.62	52.02	7.95	45.96	18.45
3	52.84	6.53	51.52	8.83	42.52	24.56
4	49.40	12.61	49.79	11.89	40.57	28.02
5	48.49	14.22	47.47	15.99	38.18	32.26
t_{90} (days)	3.44 **		3.02		1.35	

* Samples before and after storage stability test analyzed together to reduce the analytical error.

**The time required to reach 90% of the initial malathion concentration.

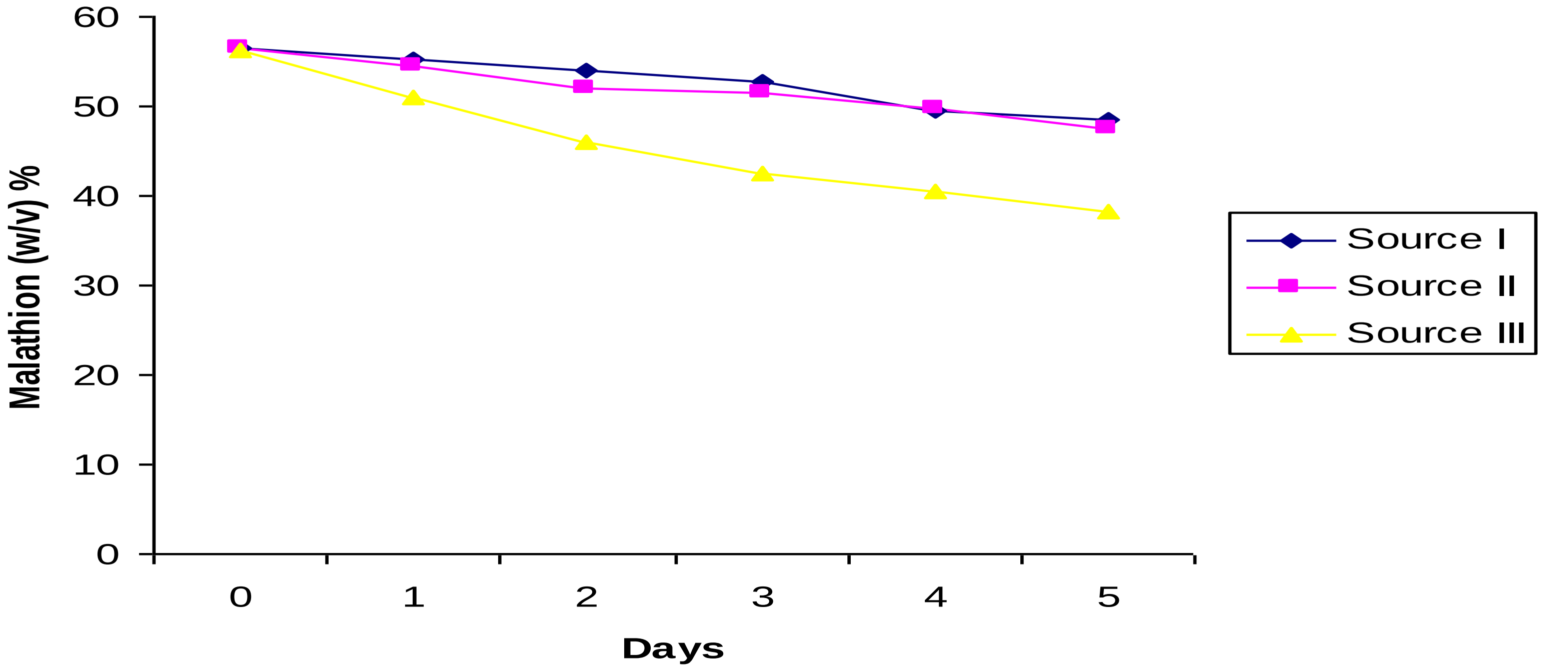


Fig. 14. Effect of storage stability on malathion 57% EC of three different manufactured sources at 72 ±2 °C.

Table 17. Effect of storage stability on malathion 57% EC of three different manufactured sources at room temperature

Storage Periods (Weeks)	**Source I**		**Source II**		**Source III**	
	Malathion content (w/v) %	**Loss %**	**Malathion content (w/v) %**	**Loss %**	**Malathion content (w/v) %**	**Loss %**
0	56.53	0	56.51	0	56.36	0
1	56.27	0.46	55.91	1.06	55.77	1.05
2	56.15	0.67	55.79	1.27	55.51	1.51
4	56.11	0.74	55.67	1.49	54.69	2.96
6	56.10	0.76	55.41	1.95	54.56	3.19
8	55.67	1.52	55.14	2.42	53.80	4.54
10	55.66	1.54	54.77	3.08	53.69	4.74
12	55.59	1.67	54.56	3.45	52.33	7.15
t_{90} (days)	528 *		252.12		119.34	

* The time required to reach 90% of the initial malathion concentration.

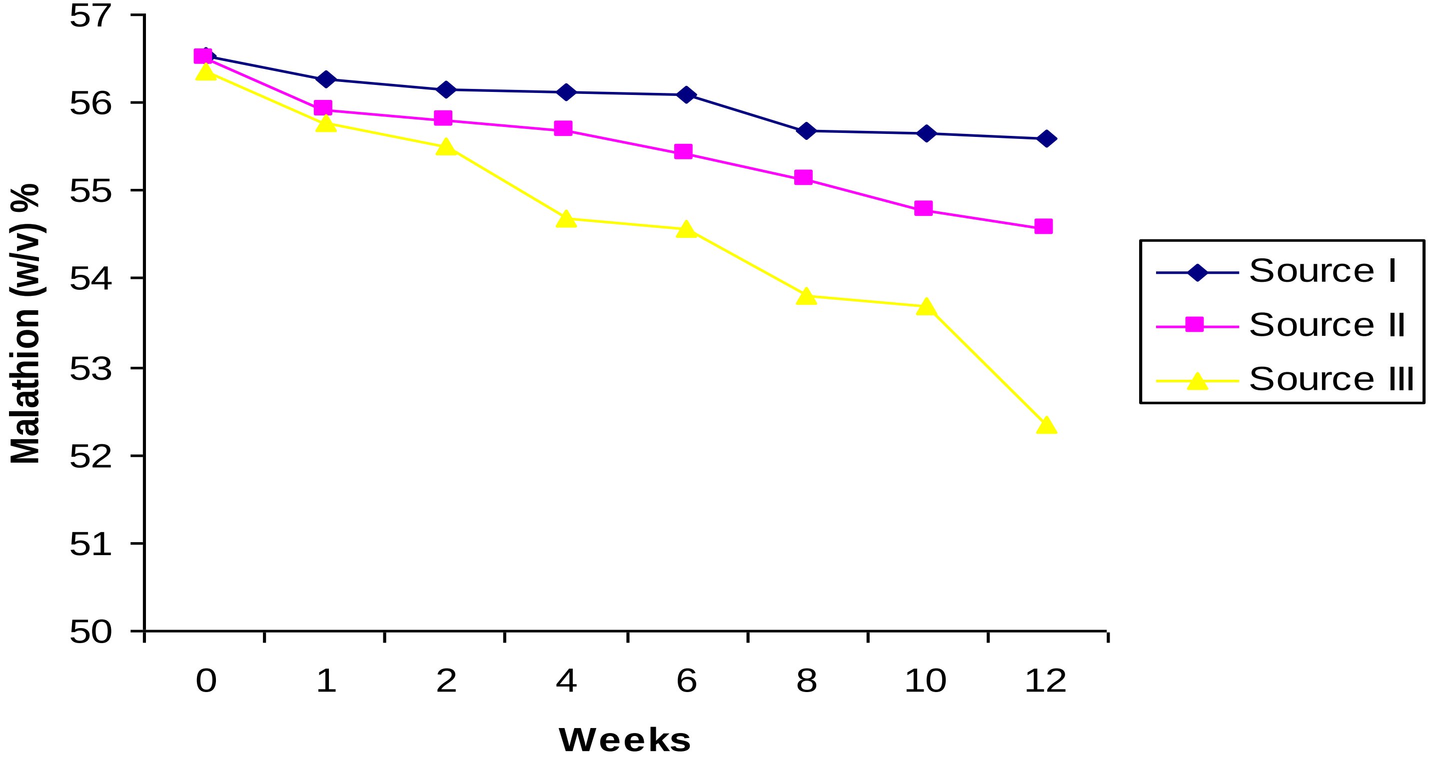


Fig. 15. Effect of storage stability on malathion 57% EC of three different manufactured sources at room temperature.

Table 18. Effect of storage on impurities of malathion at 54 ±2 °C for Source I

Storage Periods (Days)	Malathion content g/kg	Maximum of isomalathion 0.8 % of malathion found g/kg	Isomalathion found g/kg	Maximum of malaoxon 0.1% of malathion found g/kg	Malaoxon found g/kg	Maximum of MeOOSPS-triester 1.6 % of malathion found g/kg	MeOOSPS-triester found g/kg	Maximum of MeOOOPS-triester 0.5 % of malathion found g/kg	MeOOOPS-triester found g/kg
0	530.27	4.24	12.50	0.53	5.88	8.48	2.44	2.65	1.53
1	528.29	4.23	12.52	0.528	7.59	8.45	2.66	2.64	1.76
3	523.70	4.19	13.57	0.524	7.76	8.38	2.71	2.62	2.13
7	520.79	4.17	14.03	0.52	8.21	8.33	2.73	2.60	2.83
14	518.63	4.15	14.50	0.518	8.80	8.29	2.74	2.59	2.93
21	516.19	4.13	15.57	0.516	8.86	8.26	2.79	2.58	2.95

Table 19. Effect of storage on impurities of malathion at 54 ±2 °C for Source I

Compound	Impurities as g/kg of malathion content					
Days	0	1	3	7	14	21
Malathion g/kg	530.27	528.29	523.70	520.79	518.63	516.19
Isomalathion g/kg	23.57	23.70	25.91	26.94	27.97	30.16
Malaoxon g/kg	11.09	14.37	14.82	15.76	16.97	17.16
MeOOSPS-triester g/kg	4.60	5.04	5.17	5.24	5.28	5.40
MeOOOPS-triester g/kg	2.89	3.44	4.07	5.43	5.65	5.71

Table 20. Effect of storage on impurities of malathion at 72 ±2 ^{o}C for Source I

Storage Periods (Days)	Malathion content g/kg	Maximum of isomalathion 0.8 % of malathion found g/kg	Isomalathion found g/kg	Maximum of malaoxon 0.1% of malathion found g/kg	Malaoxon found g/kg	Maximum of MeOOSPS-triester 1.6 % of malathion found g/kg	MeOOSPS-triester found g/kg	Maximum of MeOOOPS-triester 0.5 % of malathion found g/kg	MeOOOPS-triester found g/kg
0	530.27	4.24	12.50	0.53	5.88	8.48	2.44	2.65	1.53
1	517.51	4.14	20.08	0.517	7.74	8.28	2.54	2.59	1.78
2	505.78	4.046	21.73	0.506	7.83	8.09	2.59	2.53	2.57
3	495.65	3.96	24.32	0.49	8.60	7.93	2.61	2.48	2.62
4	463.38	3.71	25.75	0.46	8.68	7.41	2.62	2.32	3.28
5	454.85	3.64	26.95	0.45	8.99	7.28	2.78	2.27	3.65

Table 21. Effect of storage on impurities of malathion at 72 ±2 ^{o}C for Source I

Compound	Impurities as g/kg of malathion content					
days	0	1	2	3	4	5
Malathion g/kg	530.27	517.51	505.78	495.65	463.38	454.85
Isomalathion g/kg	23.57	38.80	42.96	49.07	55.57	59.25
Malaoxon g/kg	11.09	14.96	15.48	17.35	18.73	19.76
MeOOSPS-triester g/kg	4.60	4.91	5.11	5.27	5.65	6.11
MeOOOPS-triester g/kg	2.89	3.44	5.08	5.28	7.08	8.02

Table 22. Effect of storage on impurities of malathion at room temperature for Source I

Storage Periods (Days)	Malathion content g/kg	Maximum of isomalathion 0.8 % of malathion found g/kg	Isomalathion found g/kg	Maximum of malaoxon 0.1% of malathion found g/kg	Malaoxon found g/kg	Maximum of MeOOSPS-triester 1.6 % of malathion found g/kg	MeOOSPS-triester found g/kg	Maximum of MeOOOPS-triester 0.5 % of malathion found g/kg	MeOOOPS-triester found g/kg
0	530.27	4.24	12.50	0.53	5.88	8.48	2.44	2.65	1.53
1	527.83	4.22	15.01	0.53	6.23	8.44	2.57	2.64	2.17
2	526.70	4.21	15.54	0.53	9.67	8.43	2.58	2.63	2.365
4	526.32	4.21	16.35	0.53	10.17	8.42	2.59	2.63	2.96
6	526.23	4.21	17.07	0.53	10.43	8.42	2.60	2.63	2.98
8	522.20	4.18	18.75	0.52	10.80	8.36	2.61	2.61	3.20
10	522.10	4.18	19.69	0.52	11.55	8.35	2.67	2.61	3.57
12	521.44	4.17	22.85	0.52	11.79	8.34	2.70	2.61	3.77

Table 23. Effect of storage on impurities of malathion at room temperature for Source I

Compound	Impurities as g/kg of malathion content							
Weeks	0	1	2	4	6	8	10	12
Malathion g/kg	530.27	527.83	526.70	526.32	526.23	522.20	522.10	521.44
Isomalathion g/kg	23.57	28.44	29.50	31.06	32.44	35.91	37.71	43.82
Malaoxon g/kg	11.09	11.80	18.36	19.32	19.82	20.68	22.12	22.61
MeOOSPS-triester g/kg	4.60	4.87	4.898	4.92	4.94	5.00	5.11	5.18
MeOOOPS-triester g/kg	2.89	4.11	4.49	5.62	5.66	6.13	6.84	7.23

Table 24. Effect of storage on impurities of malathion at 54 ±2 °C for Source II

Storage Periods (Days)	Malathion content g/kg	Maximum of isomalathion 0.8 % of malathion found g/kg	Isomalathion found g/kg	Maximum of malaoxon 0.1% of malathion found g/kg	Malaoxon found g/kg	Maximum of MeOOSPS-triester 1.6 % of malathion found g/kg	MeOOSPS-triester found g/kg	Maximum of MeOOOPS-triester 0.5 % of malathion found g/kg	MeOOOPS-triester found g/kg
0	522.34	4.18	9.897	0.52	19.16	8.36	2.91	2.61	1.17
1	511.89	4.095	13.67	0.51	21.86	8.19	3.15	2.56	1.37
3	510.78	4.086	14.66	0.51	26.26	8.17	3.197	2.55	1.84
7	509.40	4.075	14.75	0.51	27.27	8.15	3.31	2.55	2.16
14	494.79	3.96	15.65	0.50	30.99	7.92	3.36	2.47	2.18
21	485.27	3.88	17.25	0.49	31.20	7.76	4.39	2.43	2.53

Table 25. Effect of storage on impurities of malathion at 54 ±2 °C for Source II

Compound	Impurities as g/kg of malathion content					
days	0	1	3	7	14	21
Malathion g/kg	522.34	511.89	510.78	509.40	494.79	485.27
Isomalathion g/kg	18.95	26.70	28.70	28.96	31.71	35.55
Malaoxon g/kg	36.68	42.70	51.41	53.53	62.63	64.29
MeOOSPS-triester g/kg	5.57	6.15	6.26	6.50	6.79	9.05
MeOOOPS-triester g/kg	2.24	2.68	3.60	4.24	4.41	5.21

Table 26. Effect of storage on impurities of malathion at 72 ±2 °C for Source II

Storage Periods (Days)	Malathion content g/kg	Maximum of isomalathion 0.8 % of malathion found g/kg	Isomalathion found g/kg	Maximum of malaoxon 0.1% of malathion found g/kg	Malaoxon found g/kg	Maximum of MeOOSPS-triester 1.6 % of malathion found g/kg	MeOOSPS-triester found g/kg	Maximum of MeOOOPS-triester 0.5 % of malathion found g/kg	MeOOOPS-triester found g/kg
0	522.34	4.18	9.897	0.52	19.16	8.36	2.91	2.61	1.17
1	503.39	4.027	10.34	0.50	23.35	8.054	3.094	2.62	1.272
2	480.84	3.85	12.03	0.48	26.10	7.69	3.11	2.40	1.81
3	476.21	3.81	12.46	0.48	28.56	7.62	3.16	2.38	2.69
4	460.22	3.68	12.86	0.46	29.39	7.36	3.21	2.30	2.92
5	438.78	3.51	13.52	0.44	29.75	7.02	3.80	2.19	3.31

Table 27. Effect of storage on impurities of malathion at 72 ±2 °C for Source II

Compound / days	Impurities as g/kg of malathion content					
	0	1	2	3	4	5
Malathion g/kg	522.34	503.39	480.84	476.21	460.22	438.78
Isomalathion g/kg	18.95	20.54	25.02	26.16	27.94	30.81
Malaoxon g/kg	36.68	46.39	54.28	59.97	63.86	67.80
MeOOSPS-triester g/kg	5.57	6.15	6.47	6.64	6.97	8.66
MeOOOPS-triester g/kg	2.24	2.53	3.76	5.65	6.34	7.54

Table 28. Effect of storage on impurities of malathion at room temperature for Source II

Storage Periods (Days)	Malathion content g/kg	Maximum of isomalathion 0.8 % of malathion found g/kg	Isomalathion found g/kg	Maximum of malaoxon 0.1% of malathion found g/kg	Malaoxon found g/kg	Maximum of MeOOSPS-triester 1.6 % of malathion found g/kg	MeOOSPS-triester found g/kg	Maximum of MeOOOPS-triester 0.5 % of malathion found g/kg	MeOOOPS-triester found g/kg
0	522.34	4.18	9.897	0.52	19.60	8.36	2.91	2.61	1.17
1	516.79	4.13	10.00	0.52	20.46	8.27	3.31	2.58	2.29
2	515.68	4.13	10.798	0.52	20.67	8.25	3.44	2.58	2.39
4	514.57	4.12	11.50	0.51	23.51	8.23	3.51	2.57	2.48
6	512.17	4.10	12.34	0.51	24.95	8.19	3.56	2.56	3.10
8	509.67	4.08	12.63	0.51	26.60	8.15	3.83	2.55	3.48
10	506.25	4.05	13.78	0.51	27.91	8.10	4.02	2.53	3.53
12	504.31	4.03	14.24	0.50	29.10	8.07	4.17	2.52	4.38

Table 29. Effect of storage on impurities of malathion at room temperature for Source II

Compound	Impurities as g/kg of malathion content							
Weeks	0	1	2	4	6	8	10	12
Malathion g/kg	522.34	516.79	515.68	514.57	512.17	509.67	506.25	504.31
Isomalathion g/kg	18.95	19.35	20.94	22.35	24.09	24.78	27.22	28.24
Malaoxon g/kg	36.68	39.59	40.08	45.69	48.71	52.19	55.13	57.70
MeOOSPS-triester g/kg	5.57	6.41	6.67	6.83	6.95	7.51	7.95	8.27
MeOOOPS-triester g/kg	2.24	4.43	4.63	4.82	6.05	6.83	6.97	8.69

Table 30. Effect of storage on impurities of malathion at 54 ±2 °C for Source III

Storage Periods (Days)	Malathion content g/kg	Maximum of isomalathion 0.8 % of malathion found g/kg	Isomalathion found g/kg	Maximum of malaoxon 0.1% of malathion found g/kg	Malaoxon found g/kg	Maximum of MeOOSPS-triester 1.6 % of malathion found g/kg	MeOOSPS-triester found g/kg	Maximum of MeOOOPS-triester 0.5 % of malathion found g/kg	MeOOOPS-triester found g/kg
0	532.40	4.26	83.20	0.53	4.35	8.52	11.42	2.66	2.16
1	510.11	4.08	83.86	0.51	4.78	8.16	13.12	2.55	2.57
3	499.72	3.99	86.56	0.50	5.24	7.99	13.27	2.49	2.99
7	479.88	3.84	89.34	0.48	5.54	7.68	13.72	2.39	3.29
14	455.03	3.64	90.15	0.46	6.11	7.28	13.81	2.27	3.55
21	415.83	3.33	90.75	0.42	7.097	6.65	13.95	2.08	3.74

Table 31. Effect of storage on impurities of malathion at 54 ±2 °C for Source III

Compound	Impurities as g/kg of malathion content					
days	0	1	3	7	14	21
Malathion g/kg	532.40	510.11	499.72	479.88	455.03	415.83
Isomalathion g/kg	156.27	164.39	173.22	186.17	198.12	218.24
Malaoxon g/kg	8.17	9.37	10.49	11.54	13.43	17.08
MeOOSPS-triester g/kg	21.45	25.72	26.55	28.59	30.35	33.55
MeOOOPS-triester g/kg	4.06	5.04	5.98	6.86	7.80	9.00

Table 32. Effect of storage on impurities of malathion at 72 ±2 °C for Source III

Storage Periods (Days)	Malathion content g/kg	Maximum of isomalathion 0.8 % of malathion found g/kg	Isomalathion found g/kg	Maximum of malaoxon 0.1% of malathion found g/kg	Malaoxon found g/kg	Maximum of MeOOSPS-triester 1.6 % of malathion found g/kg	MeOOSPS-triester found g/kg	Maximum of MeOOOPS-triester 0.5 % of malathion found g/kg	MeOOOPS-triester found g/kg
0	532.40	4.26	83.20	0.53	4.35	8.52	11.42	2.66	2.16
1	480.63	3.85	86.03	0.48	6.20	7.69	12.70	2.40	2.86
2	434.16	3.47	90.63	0.43	6.87	6.95	13.20	2.17	3.51
3	401.66	3.21	92.60	0.40	6.92	6.43	13.41	2.01	4.11
4	383.24	3.06	93.67	0.38	7.29	6.13	14.23	1.92	4.77
5	360.66	2.88	98.61	0.36	8.78	5.77	15.13	1.80	5.61

Table 33. Effect of storage on impurities of malathion at 72 ±2 °C for Source III

Compound	Impurities as g/kg of malathion content					
days	0	1	2	3	4	5
Malathion g/kg	532.40	480.63	434.16	401.66	383.24	360.66
Isomalathion g/kg	156.27	178.99	208.75	230.54	244.42	273.42
Malaoxon g/kg	8.17	12.90	15.82	17.23	19.02	24.34
MeOOSPS-triester g/kg	21.45	26.42	30.40	33.39	37.13	41.95
MeOOOPS-triester g/kg	4.06	5.95	8.08	10.23	12.45	15.55

Table 34. Effect of storage on impurities of malathion at room temperature for Source III

Storage Periods (Days)	Malathion content g/kg	Maximum of isomalathion 0.8 % of malathion found g/kg	Isomalathion found g/kg	Maximum of malaoxon 0.1% of malathion found g/kg	Malaoxon found g/kg	Maximum of MeOOSPS-triester 1.6 % of malathion found g/kg	MeOOSPS-triester found g/kg	Maximum of MeOOOPS-triester 0.5 % of malathion found g/kg	MeOOOPS-triester found g/kg
0	532.40	4.26	83.20	0.53	4.35	8.52	11.42	2.66	2.16
1	526.83	4.21	84.20	0.53	5.30	8.43	11.73	2.63	2.53
2	524.37	4.19	89.11	0.52	5.36	8.39	12.33	2.62	3.08
4	516.63	4.13	89.62	0.52	5.38	8.27	12.95	2.58	3.39
6	515.40	4.12	90.63	0.52	5.81	8.25	13.17	2.58	3.62
8	508.22	4.06	91.79	0.51	5.84	8.13	14.02	2.54	4.03
10	507.18	4.05	93.20	0.51	6.11	8.11	14.61	2.53	4.097
12	494.33	3.95	94.86	0.50	6.13	7.91	14.68	2.47	4.20

Table 35. Effect of storage on impurities of malathion at room temperature for Source III

Compound	Impurities as g/kg of malathion content							
Weeks	0	1	2	4	6	8	10	12
Malathion g/kg	532.40	526.83	524.37	516.63	515.40	508.22	507.18	494.33
Isomalathion g/kg	156.27	159.82	169.94	173.47	175.84	180.61	183.76	191.89
Malaoxon g/kg	8.17	10.06	10.22	10.41	11.27	11.50	12.05	12.40
MeOOSPS-triester g/kg	21.45	22.27	23.51	25.07	25.55	27.59	28.81	29.70
MeOOOPS-triester g/kg	4.06	4.80	5.87	6.56	7.02	7.93	8.08	8.50

Table 36. Impurities in technical malathion

Technical	Malathion content g/kg	Isomalathion found g/kg	Isomalathion as g/kg of malathion content	Malaoxon found g/kg	Malaoxon as g/kg of malathion content	MeOOSPS-triester found g/kg	MeOOSPS-triester as g/kg of malathion content	MeOOOPS-triester found g/kg	MeOOOPS-triester as g/kg of malathion content
I	943.60	18.00	19.08 *	1.64	1.74 **	5.68	6.02 ***	0.10	0.106 ****
II	940.20	32.96	35.06	1.265	1.35	3.95	4.20	1.315	1.40
III	954.70	22.50	23.57	1.34	1.40	3.36	3.52	0.45	0.47

* Maximum level of isomalathion in technical = 4 g/kg

** Maximum level of malaoxon in technical = 1 g/kg

*** Maximum level of MeOOSPS-triester = 15 g/kg

****Maximum level of MeOOOPS-triester =5 g/kg

Table 37. Emulsion stability and re-emulsification for malathion 57% EC after storage at 54 ±2 ^{o}C by using CIPAC standard water D.

Storage Periods (Days)	**Source I**			**Source II**			**Source III**		
	0.5 h	2 h	24.5 h	0.5 h	2 h	24.5 h	0.5 h	2 h	24.5 h
0	– *	–	–	3.75 **	8.8	6.8	3.5	6.5	3.5
1	–	–	–	4.7	8.1	6.8	1.9	5.7	–
3	–	–	–	4.5	7.4	4.4	2.7	7.3	–
7	–	–	–	3.7	6.8	3.6	0.6	4.5	–
14	–	–	–	2.6	6.6	3.5	–	1.25	–
21	–	–	–	1.5	4.8	–	–	–	–

Table 38. Emulsion stability and re-emulsification for malathion 57% EC after storage at 72 ±2 ^{o}C by using CIPAC standard water D

Storage Periods (Days)	**Source I**			**Source II**			**Source III**		
	0.5 h	2 h	24.5 h	0.5 h	2 h	24.5 h	0.5 h	2 h	24.5 h
0	– *	–	–	3.75 **	8.8	6.8	3.5	6.6	3.5
1	–	–	–	5.5	8.7	6	4.3	6.7	–
2	–	–	–	4.6	7.8	4.7	1.95	5.8	–
3	–	–	–	3.3	6.45	1.2	–	–	–
4	–	–	–	1.8	5.5	0.6	–	–	–
5	–	–	–	0.7	3.6	–	–	–	–

* No precipitate

** Volume of precipitate by ml

Table 39. Emulsion stability and re-emulsification for malathion 57% EC after storage at room temperature by using CIPAC standard water D

Storage Periods (weeks)	**Source I**			**Source II**			**Source III**		
	0.5 h	2 h	24.5 h	0.5 h	2 h	24.5 h	0.5 h	2 h	24.5 h
0	– *	–	–	3.75 **	8.8	6.8	3.5	6.6	3.5
1	–	–	–	4	8.8	7.1	3.8	6.8	4.2
2	–	–	–	4.3	8.8	7.4	4.25	7	4.9
4	–	–	–	4.5	8.9	7.7	4.6	7.2	5.6
6	–	–	–	4.9	9	8.1	5	7.3	6.3
8	–	–	–	5.1	9	8.4	5.4	7.5	7
10	–	–	–	5.35	9.1	8.7	5.8	7.7	8
12	1.1	4	0.2	5.7	9.1	9	6.2	8	8.5

* No precipitate

** Volume of precipitate by ml

Table 40. acidity of malathion after storage at 54 ±2 °C

Storage Periods (Days)	**Source I**	**Source II**	**Source III**
	g/kg *	**g/kg ***	**g/kg ***
0	1.67	5.11	6.83
1	1.77	5.3	7.05
3	2.07	5.4	7.56
7	2.49	5.95	7.86
14	3.19	6.55	8.13
21	4.03	7.01	8.49

* Acidity g/kg calculated as H_2SO_4

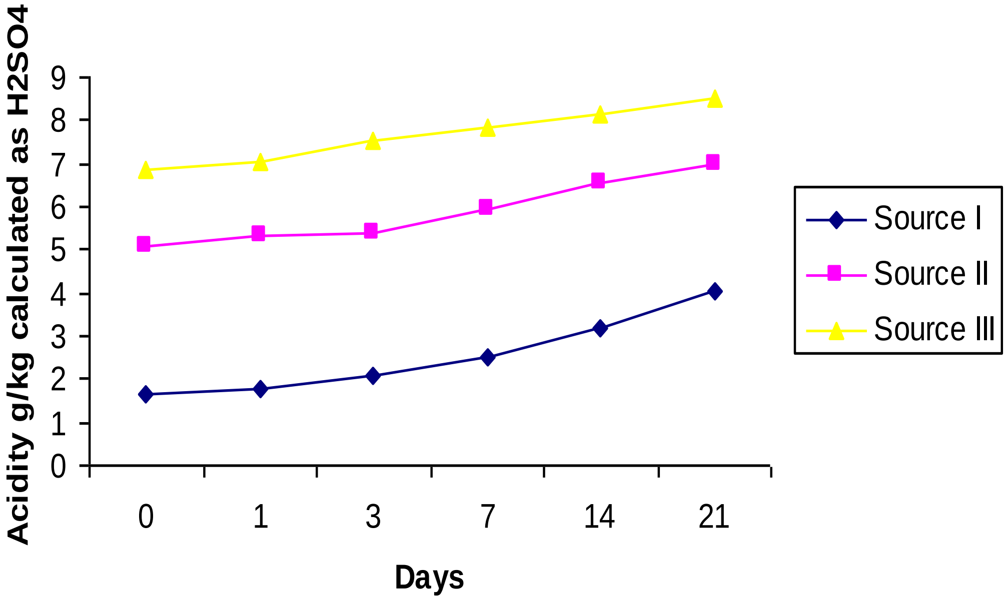


Fig. 16. Acidity of malathion after storage at 54 ±2 °C

Table 41. acidity of malathion after storage at 72 ±2 °C

Storage Periods (Days)	Source I	Source II	Source III
	g/kg *	g/kg *	g/kg *
0	1.67	5.11	6.83
1	2.54	5.66	8.01
2	3.16	5.71	8.52
3	3.73	6.92	8.98
4	4.16	7.07	9.44
5	4.63	7.22	9.94

* Acidity g/kg calculated as H_2SO_4

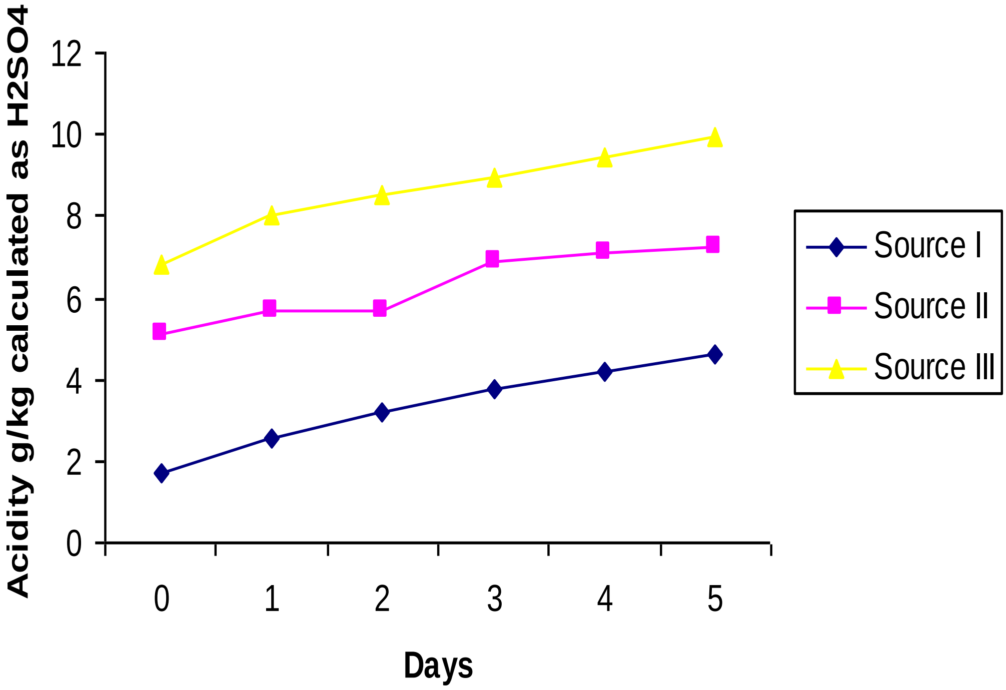


Fig. 17. Acidity of malathion after storage at 72 ±2 °C

Table 42. acidity of malathion after storage at room temperature

Storage Periods (Days)	**Source I**	**Source II**	**Source III**
	g/kg *	**g/kg ***	**g/kg ***
0	1.67	5.11	6.83
1	2	5.72	7.35
2	2.32	6.33	7.87
4	2.64	6.94	8.39
6	2.97	7.55	8.91
8	3.29	8.16	9.43
10	3.45	8.77	9.95
12	3.62	9.38	10.46

* Acidity g/kg calculated as H_2SO_4

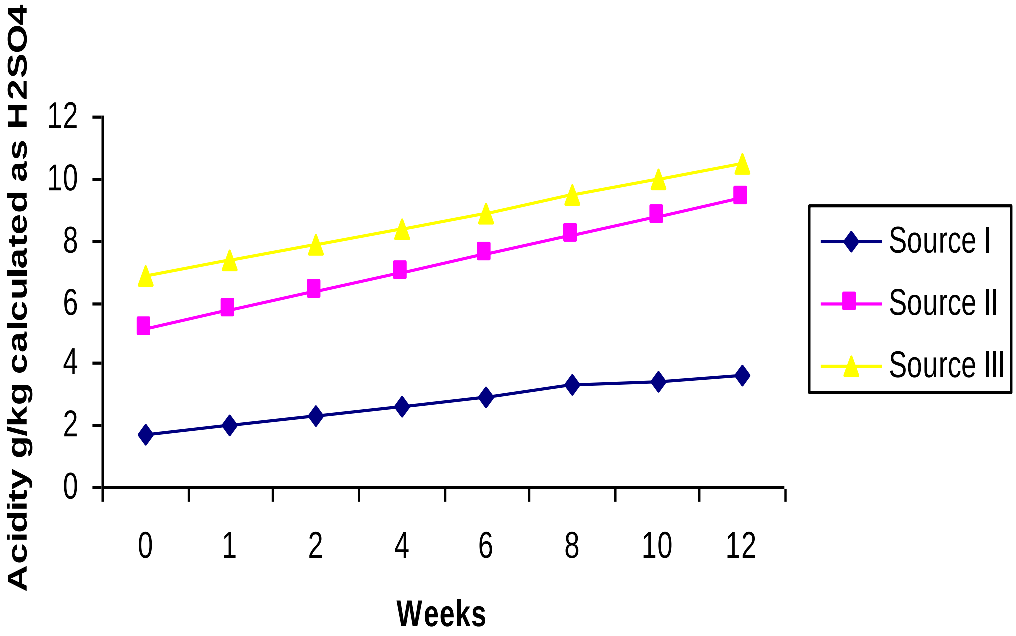


Fig. 18. Acidity of malathion after storage at room temperature