

The Quality of Chlorpyrifos Emulsifiable Concentrate Formulations

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A STUDY was conducted to investigate the degradation of chlorpyrifos, as well as studying the formation of its impurity sulfotep after storage at $54 \pm 2^\circ\text{C}$ for 1, 3, 7, 14, 21 days, at $72 \pm 2^\circ\text{C}$ for 1-5 days, and at room temperature within range 1-12 weeks of three commercial chlorpyrifos Emulsifiable Concentrate (EC) formulations (48% w/v) from the Egyptian market (manufactured from three different companies). The obtained results showed that chlorpyrifos was more stable after storage at $54 \pm 2^\circ\text{C}$ and at room temperature, whereas the rate of degradation increased after storage at $72 \pm 2^\circ\text{C}$. There is no difference on the rate of degradation for all chlorpyrifos formulations under investigation. The sulfotep content of the three commercial formulations didn't show any correlation with storage temperature and storage time. However, in one of the commercial formulations of chlorpyrifos, the sulfotep content was more than the maximum permissible concentration of impurity recommended by FAO Specifications for chlorpyrifos (2008).

Keywords: Chlorpyrifos, Degradation and Sulfotep.

Chlorpyrifos [*O,O*-diethyl-*O*-3,5,6-trichloro-2-pyridyl phosphorothioate] is an organophosphorus pesticide (OPP), which is a broadly active insecticide effective by ingestion and contact. The metabolites of chlorpyrifos being chlorpyrifos oxon, 3, 5, 6-trichloro-2-pyridinol and diethyl phosphorothioic acid and/or diethyl phosphoric acid^(1,2). Chlorpyrifos is stable in air (non volatile) and it is not sensitive to ultra violet radiation. It is stable to neutral and weakly acidic solution, but it is hydrolysed by strong bases. The rate of chlorpyrifos hydrolysis increases with both pH and temperature⁽³⁾. The effect of accelerated storage at $54 \pm 2^\circ\text{C}$ on chlorpyrifos and pirimiphos-methyl, indicated that the latter was more degraded than chlorpyrifos⁽⁴⁾. Technical chlorpyrifos can contain two interesting impurities and/ or breakdown products, sulfotep [*O, O, O, O*-tetraethyl dithiopyrophosphate] and 3, 5, 6-trichloro pyridinol, the later is significant from a toxicological viewpoint⁽⁵⁾. According to FAO Specifications and Evaluations for chlorpyrifos (2008), sulfotep is the main impurity in chlorpyrifos (technical and formulations), it should not be higher

than 3g/kg for technical chlorpyrifos, and 0.3 % of chlorpyrifos content in all formulations of chlorpyrifos. Sulfotep is a highly toxic impurity that may be present in trace quantities in chlorpyrifos⁽⁶⁾. Since sulfotep has been shown formed during the manufacturing process⁽⁷⁾ and it is not hydrolysis product⁽⁸⁾.

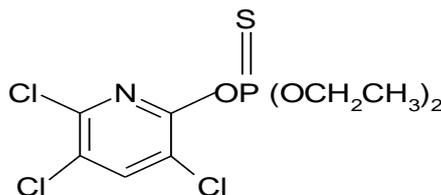
The aim target of this work is to investigate and study the stability of three commercial chlorpyrifos emulsifiable concentrate formulations (48% w/v) from the Egyptian market (manufactured in three different companies), and the formation of its impurity sulfotep after storage at different intervals of temperature and time.

The structure and characterization of the investigated chlorpyrifos and their impurity sulfotep are shown in Fig. 1.

• Chlorpyrifos

IUPAC Name: *O,O*-diethyl-*O*-3,5,6-trichloro-2-pyridyl phosphorothioate.

Structural Formula:



Molecular Formula: C₉H₁₁Cl₃NO₃PS

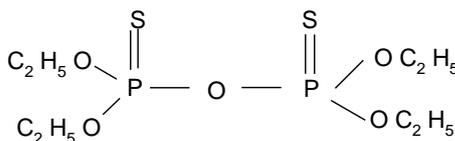
Relative Molecular mass: 350.6

CAS Registry number: 2912-88-2

• Sulfotep as Impurity

IUPAC Name: *O, O, O, O*-Tetraethyl dithiopyrophosphate

Structural Formula:



Molecular formula: C₈H₂₀O₅P₂S₂

Relative Molecular mass: 322.32

CAS Registry number : 3689-24-5

Fig. 1.

Experimental

Materials

Chlorpyrifos: analytical standard 99.4% from AAKO company - Netherlands. Sulfotep analytical standard 97.1%: from Chem. Service. Methanol: (MERCK). Isooctane: GR for analysis (MERCK).

Chlorpyrifos 48% (w/v) emulsifiable concentrate (EC) commercial formulation was obtained from three different Manufacture sources in Egypt (Manufactured in three different companies).

Procedure

Accelerated storage procedure⁽⁹⁾

Place the emulsifiable concentrate (about 50 ml) in the bottle. Cap the bottle and put it in the oven for specified time and temperature. At the end of the time, remove the bottle from the oven, remove the cap, and allow the bottle and contents to cool naturally to room temperature, replacing the cap when cool.

- Storage at 54 ± 2 °C for 1, 3, 7, 14, 21 days.
- Storage at 72 ± 2 °C for 1, 2, 3, 4, 5 days.
- Storage at room temperature for 1, 2, 4, 6, 8, 10, 12 weeks.

Preparation of samples

Chlorpyrifos

Standard preparation: Weight 10 mg of chlorpyrifos analytical standard inside a 25ml volumetric Flask then dissolve it and complete to the final volume with methanol.

Sample preparation: Accurately weight sufficient sample material formulation 48% w/v to equivalent 10 mg of chlorpyrifos standard in a 25 ml volumetric Flask mix slowly with methanol and complete the volume with methanol.

Sulfotep

Standard preparation: Weight 10 mg of sulfotep analytical standard inside a 10 ml volumetric Flask dissolve it with isooctane and complete the volume with isooctane.

Sample preparation: Accurately weight sufficient sample material formulation to contain approximately 0.3 gm chlorpyrifos in 10 ml volumetric flask, dissolve it with isooctane and complete the volume with isooctane.

Measurements

Gas chromatography determination for chlorpyrifos and sulfotep

A Hewlett-Packard 6890 gas chromatograph equipped with Flame Ionization Detector (FID) at 275 °C, capillary column HP-50% (15 m x 0.53 mm I.D., 1 µm film thickness). Nitrogen was used as a carrier gas at 20 ml/min.

The oven temperature program was held at 180 °C for 1 min, then ramp 10 °C /min to 250 °C, and kept at that temperature for 5 min. Injector temperature was 225 °C. The injection volume was 1 µl. typical retention time of chlorpyrifos was 4.2 min and sulfotep was 1.9 min.

Gas chromatography-mass spectrometry analysis of chlorpyrifos

The GC-MS analysis was performed with an Agilent 6890 gas chromatograph equipped with an Agilent mass spectrometric detector, with a direct capillary interface and fused silica capillary column HP-5MS(30 m x 320 µm x 0.25 µm film thickness). Helium was used as carrier gas at approximately 1.0 ml/min pulsed splitless mode. The solvent delay was 3 min, and the injection volume was 1 µl. The mass spectrometric detector was operated in electron impact ionization mode with an ionizing energy of 70 e.v scanning from m/z 50 to 500. The ion source temperature was 230 °C and the quadruple temperature 150 °C. The electron multiplier voltage (EM voltage) was maintained 1050 v above auto tune. The instrument was manually tuned using perfluorotributyl amine (PFTBA). The GC temperature program was held at 80 °C for 3 min, then elevated to 260 °C at rate of 8 °C/min, the detector and injector temperatures were set at 280 and 250 °C, respectively.

Results and Discussion

Effect of storage stability on chlorpyrifos 48% EC content

The data from Table 1, showed that the effect of storage at 54 ±2 °C on three commercial chlorpyrifos formulations indicated that, chlorpyrifos has not been changed by storage at 54 ±2 °C for 14, 21 days, where the percentage of loss after 21 days was 3.85, 4.46 and 3.75 % for sources I, II and III, respectively. However chlorpyrifos was more stable after storage at room temperature 25 °C and Table 2 showed that the percentage of loss after 12 weeks was 2.12, 2.97 and 2.31% for sources I, II, and III, respectively, but Table 3 showed that the percentage of loss after storage at 72 ±2 °C for 5 days was 11.12, 12.30 and 12.35% for source I, II, and III, respectively. The stability of chlorpyrifos after storage at 72 ±2 °C for 5 days was less stable from storage at 25 °C and 54 ±2 °C. The previously mentioned results clearly showed that the rate of degradation of the three chlorpyrifos formulations under investigation were influenced by change in temperature degrees and long period of storage. In general increasing temperature degrees increased the rate of degradation. 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 are in accordance with Smith ⁽¹⁰⁾, this can be shown according to the following equation:

TABLE 1. Effect of storage stability on chlorpyrifos 48% w/v EC of three different manufacture sources at 54 ± 2 °C for 1, 3, 7, 14, 21 days.

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

TABLE 2. Effect of storage stability on chlorpyrifos 48% w/v EC of three different manufacture sources at room temperature for 1, 2, 4, 6, 8, 10, 12 weeks.

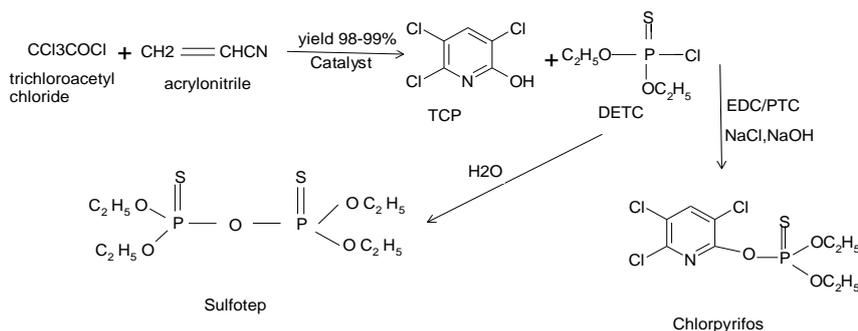
Storage periods (Weeks)	Source I		Source II		Source III	
	Chlorpyrifos content (w/v) %	Loss %	Chlorpyrifos content (w/v) %	Loss %	Chlorpyrifos content (w/v) %	Loss %
0	47.02	0	47.09	0	47.2	0
1	46.87	0.32	46.86	0.49	47.14	0.13
2	46.78	0.51	46.76	0.70	46.77	0.91
4	46.75	0.57	46.47	1.32	46.64	1.19
6	46.68	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

TABLE 3. Effect of storage stability on chlorpyrifos 48% w/v EC of three different manufacture sources at 72 ± 2 °C for 1, 2, 3, 4, 5 days.

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

Effect of storage stability on the formation of sulfotep

The data from Table 4 showed the effect of storage at $54 \pm 2^\circ\text{C}$ for 1, 3, 7, 14, 21 days, and $72 \pm 2^\circ\text{C}$ for 1, 2, 3, 4, 5 days on the formation of sulfotep. We found that the formation of sulfotep was not affected by storage at 54°C and 72°C and that for the three manufactured sources of chlorpyrifos I, II and III, and also sulfotep formation was not affected by storage at room temperature according to Table 5. Also, sulfotep found from source I and III was in allowed limits according to FAO specifications for chlorpyrifos (2008) where the maximum level of sulfotep in chlorpyrifos 48% EC is 0.3% of chlorpyrifos content, but the results from source II the sulfotep found was more than the allowed limits according to FAO specifications and that was found before storage and after storage at 25°C , $54 \pm 2^\circ\text{C}$ and $72 \pm 2^\circ\text{C}$. This may be attributed to the manufacturing process⁽¹³⁾, that sulfotep can be produced as byproduct from hydrolysis of diethyl thionyl phosphoryl chloride (DETC)⁽¹⁴⁾ according to the following equation:



Also, these obtained results were in agreement with Allender & James⁽⁵⁾ who reported that the sulfotep content of the commercial products did not show any correlation with storage time.

TABLE 5. Effect of storage on the amount of sulfotep in chlorpyrifos 48 % w/v EC from three different manufactured sources at room temperature) for 1, 2, 4, 6, 8, 10, 12 weeks.

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

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مدى جودة مستحضرات الكلوربيريفوس القابلة للاستحلاب

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أجريت هذه الدراسة لبحث تكسير الكلوربيريفوس ومدى تكوين شائبته سلفوتب بعد التخزين عند درجة حرارة 54م[±] 2 لمدة 1، 3، 7، 14، 21 يوم وعند درجة حرارة 72م[±] 2 لمدة 1، 2، 3، 4، 5 يوم وعند درجة حرارة الغرفة لمدة 1، 2، 4، 6، 8، 10، 12 أسبوع وذلك لثلاثة مستحضرات قابلة للاستحلاب من الكلوربيريفوس 48٪ من ثلاثة شركات مختلفة في مصر. النتائج المتحصل عليها تشير الى أن الكلوربيريفوس كان أكثر ثباتا عند درجة حرارة الغرفة وعند 54م[±] 2 بينما كان معدل الانحدار في المادة الفعالة أكثر بعد التخزين عند 72م[±] 2 وايضا أنه لا يوجد أي اختلاف في معدل انحدار الكلوربيريفوس بالنسبة للثلاثة مستحضرات المستخدمة في البحث. وبالنسبة لمحتوى السلفوتب لم يتأثر سواء بارتفاع درجة الحرارة أو طول مدة التخزين على الرغم من أن أحد هذه المستحضرات التجارية الثلاثة كانت نسبة السلفوتب فيه أكثر من الحد الأقصى المسموح به بالنسبة لمواصفات منظمة الأغذية والزراعة FAO بالنسبة للكلوربيريفوس (2008).