Studies on Physico-Chemical Properties of Commercially Available EC Formulations Of Cypermethrin and Chlorpyrifos Pesticides .

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Abstract:

In present studies of the physico-chemical properties of various commercially available EC formulations of cypermethrin and chlorpyrifos insecticides, which are widely used for plant protection from insect pests were investigated. As per BIS specifications available for cypermethrin and chlorpyrifos, physical and chemical properties were determined. The results of the present studies are further utilized for selection and also for agricultural application. The present studies are also focused on quality of commercially available formulations of insecticides. This present study may help the researchers as a guideline for analysis of pesticide formulation and to predict the standards of commercial formulations.

Key words: Cypermethrin, Chlorpyrifos, physico-chemical properties, EC formulation, BIS specifications .

1.1 Introduction:

Use of synthetic pesticides has become a wide spread practice, in order to prevent, control and destroy pests in better manner. Thus pesticides play an important role in crop protection. About 40million hectors of land is under cultivation in India and approximately 2.5 million tons of pesticides are used in agriculture annually throughout the world [1]. Whereas India currently uses 43178 M.T. technical grade pesticides [2] out of which 70% of the pesticides belong to insecticides. Majority of the insecticides used belong to chlorinated hydrocarbon, organo-phosphates, carbamates and synthetic pyrethroids. In India context, farmers have been using pesticides frequently to have higher yields, but injudicious use of the pesticides give rise to different problems like development of resistance in pests to pesticides , various diseases in crops , suppression in population of beneficial flora and fauna and pesticide residues in food and environment [3].

Several formulations of pesticides which are used as insecticides are commercially available as EC (emulsifiable concentrate), dust, wettable powder. However their quality and performance is the major constrained faced by the users. With this background, commercially available and widely used formulations of Cypermethrin [(RS)- α-cyano-3-phenoxybenzyl(1RS, RS,1RS,3SR)-3-(2,2-dichlorvinyl)-2,2-dimethylcyclopropanecarboxylate] and Chlorpyrifos (O,O- diethyl O-3,5,6-trichloro-2-yridylphosphorothionate)

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insecticides were tested and studied as per BIS specification. Cypermethrin is available as an emulsifiable concentrate or wettable powder [4] whereas Chlorpyrifos is available as emulsifiable concentrate, dust,pellet, spray, granular and wettable powder [5]. Physico-chemical properties of the EC formulations are assessed to ensure that the product can be safely and efficiently applied.

Cypermethrin and Chlorpyrifos are broad-spectrum pesticide, displaying insecticidal activity against a wide range of insect and arthropod pests [6,7]. Cypermethrin [(RS)- α-cyano-3-phenoxybenzyl(1RS, 3RS,1RS,3SR)-3-(2,2-dichlorvinyl)-2,2-dimethylcyclopropanecarboxylate] and Chlorpyrifos (O,O- diethyl O-3,5,6-trichloro-2-yridylphosphorothionate) formulations are available as emulsifiable concentrates (EC), baits, granules, ultra-low volumes (ULV), liquid concentrates (LC), wettable powders (WP) and dusts in the market.

The mode of chlorpyrifos action is non-systemic, and exposure of insects to the active (via contact, ingestion and/or inhalation) affects the nervous system by inhibiting the activity of acetyl cholinesterase [8]. Cypermethrin is a synthetic pyrethroid and a permethrin analogue. This group of chemicals acts primarily on the basal ganglia of the central nervous system, causing repetitive nerve action through prolongation of sodium permeability during the recovery phase of the action potential of neurons [9].

Commercially available and widely used EC formulations of cypermethrin and chlorpyrifos were assessed for their physico-chemical properties as per BIS specification in order to know their standard. To assess these properties, different samples of commercial EC formulation of cypermethrin and chlorpyrifos were collected from local market and tested in the laboratory as among different formulations of these insecticides EC formulations are widely used.

1.2 Material Method:

According to BIS specification the samples were tested for important physical tests like cold test, flashpoint, emulsion stability and chemical tests like active ingredient and acidity/alkalinity [10]. Thus various samples from different manufacturers were subjected to study to physic-chemical properties.

1.2.1 Physical Tests: Following tests were carried out on the collected samples of cypermethrin and chlorpyrifos.

1. **Cold test:**

Procedure: 50ml sample was taken in clean, transparent container and closed it with cork/stopper fitted with thermometer. The sample was cooled to 10^0c by placing the container in ice cold water. The sample was stirred at short intervals for 1 hour maintaining the temperature of sample at 10^0c. At the end of one hour, examined the material for any turbidity or separated solid or oily matter or both.

2. **Flash Point:**

Procedure: Using Abel apparatus, samples were tested for their flash point. In the method f sample under test was

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placed in the cup of the Abel apparatus and heated at a prescribed rate. A small test flame is directed into the cup at regular intervals, and the flash point was noted as the lowest temperature at which application of test flame causes the vapour above the sample to ignite with a distinct flash inside the cup.

The flash point of the sample should be above 24.5^0c.

3. Emulsion stability:

2ml sample was taken in clean, transparent container. Standard hard water (dissolve0.304g of calcium chloride anhydrous and 0.139g of magnesium chloride hexa hydrate in distilled water and make up to 1 litre) poured at 30^0c to sample at the rate of 15 to 20 ml/min. During addition, the contents of the beaker were stirred continuously with the glass rod and when the volume of diluted emulsion in the beaker reaches 100ml then addition of standard hard water was stopped. The diluted emulsion was immediately transferred to clean and dry graduated cylinder. The cylinder was kept with the content for 1 hr. at 30^0c.

After 1 hr., the volume of the creamed matter at the top and sediment at the bottom, if any was noted.

1.2.2 Chemical Tests:

1. Acidity/alkalinity test:

Qualitative Test:

About 0.5ml of sample was taken in a test tube and mixed with about one mililitre of water. The mixture was tested for acidity or alkalinity with litmus paper. (Determined as the case may be, acidity or alkalinity.)

All the collected samples were found to be acidic and therefore their acidity was determined.

Determination of Acidity:

10g of sample was weighed accurately into a dry conical flask and diluted with 100ml water. The contents of the flask were titrated immediately with the standard sodium hydroxide solution using methyl red or bromocresol purple as the indicator.

A blank reading with 100ml. of water was also determined.

Calculations:

Acidity (as H_2SO_4) percent by mass = $\frac{4.9\,(V-v)N}{M}$

[Where, V= volume in ml of standard sodium hydroxide solution required for the test,

v= volume in ml of standard sodium hydroxide solution required for the blank determination.

N= normality of standard sodium hydroxide solution

M= mass in g of the material taken for the test.]

When samples were tested by above prescribed method, acidity should be 0.05percent by mass maximum

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2. Active ingredient test:

For cypermethrin and chlorpyrifos insecticide ,GLC unit with FID was used for this determination.

A] Active ingredient test: Cypermethrin

For cypermethrin in GLC unit with FID, using solutions containing known amount of the standard cypermethrin and internal standard , the response factor, RF, for cypermethrin and internal standard was arrived at. A solution containing a known mass of sample solution and internal standard was injected subsequently into GLC unit. The percentage of cypermethrin was then calculated by standard relationship.

In GLC unit with FID the column used was 75cm×3mm id, stainless steel packed with 3 percent Dexil 300 on chromosorb W-HP, 100-120 mesh and Carrier gas (N_2) 40ml/min and fuel gas (H_2) 40ml/min along with internal standard dicyclohexyl phthalate. During sample testing temperatures were maintained as per BIS as temperature of column oven 240^0C, detector 270^0C and of injection port 270^0C[11].

Procedure: 7.5gm of sample was weightedin 25ml volumetric flask and made up to volume with toluene. From this solution 6ml were pipette out in another 25ml volumetric flask to which 5ml internal standard was added and was mixed well and made up the volume with toluene. 1.0 µl of this solution was injected in GLC.

From the print out, peak areas of cypermethrin and internal standard peaks were noted down for calculating the percentage.

Calculation:

Cypermethrin content, percentage by mass = $\frac{RF \times A1 \times m1}{A2 \times m2} \times 100$

[Where, RF = response factor; A1= area of the cypermethrin peak in the sample;

m1= mass in gm of internal standard added; A2= area of the internal standard peak; and

m2= mass in gm of the sample taken for the test.]

B] Active ingredient test: Chloropyrifos

Chloropyrifos was determined by isothermal Gas chromatography using internal standard technique.

For chlorpyrifos in GLC unit with FID, column used is 180cm×4mm id, stainless steel packed with 3 percent Ov-17on chromosorb W-HP, 80-100 mesh. Carrier gas (N_2) 30ml/min and fuel gas (H_2) 40ml/min along with internal standard dibutyl phthalate[12].

Procedure: a) Internal standard solution was prepared by weighing 0.9gm of dibutyl phthalate into 250ml volumetric flask and make up to the volume with acetone.

b) Then for preparing standard solution 0.11gm of chloropyrifos reference

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standard was weighed into 25ml volumetric flask, to which 10ml of internal standard solution was added and then volume was made up to 25ml with acetone.

c)Sample solution was prepared similar to standard solution only difference was instead of reference standard sample was used in the preparation.

- d) Initially standard solution was injected repeatedly, until the area ratio of reference substance and internal standard of two successive injections did not deviate from each other by more than 2 percent. After that sample was injected. The sequence of injection to be followed was CS_1, CS_2, CS_3 ------ (where C = standard solution and S_1 = sample solution)

Calculation: From the chromatograms of standard solution and sample solution, peak area of chloropyrifos and internal standard peak was measured from which percentage of chloropyrifos was calculated.

Chloropyrifos, percentage by mass = $\frac{M1\times A3\times A2\times P1}{M2\times A4\times A1}$

(Where, M1=area of chloropyrifos peak in the chromatogram of standard solution,

A2= area of chloropyrifos peak in the chromatogram of sample solution,

A3=area of internal standard peak in the chromatogram of standard solution,

A4= area of internal standard peak in the chromatogram of sample solution,

M1= mass of chloropyrifos in standard solution in gm.,

M2= mass of sample taken for test in gm. And P1= percentage purity of chloropyrifos reference standard.)

1.3 Results of physic-chemical properties:

1.3.1 A] Result of the various physical and chemical tests performed on different samples of cypermethrin collected are as follow:

Samples of cypermethrin (EC25)

Sample	Test performed	Result	Standard result
X1	Cold test	No turbidity	*No turbidity or separation of solid
	Emulsion stability	No creaming	▪Any separation including creaming at top and sedimentation at bottom shall not exceed 2.0ml
	Flash point	42^0c	▪Shall be above 24.5^0C
	Acidity	0.0147	▪Shall be not more than0.25percent by mass
	Active ingredient (A.I.)	24.31	▪Shall not differ from the declared value by more

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			than the percent tolerance limits
X2	Cold test Emulsion stability Flash point Acidity Active ingredient (A.I.)	No turbidity No creaming 32^0c 0.098 25.36	*No turbidity or separation of solid ▪Any separation including creaming at top and sedimentation at bottom shall not exceed 2.0ml ▪Shall be above 24.5^0C ▪Shall be not more than0.25percent by mass ▪Shall not differ from the declared value by more than the percent tolerance limits
X3	Cold test Emulsion stability Flash point Acidity Active ingredient (A.I.)	No turbidity Small amount of sediment 45^0c 0.02205 ---------	*No turbidity or separation of solid ▪Any separation including creaming at top and sedimentation at bottom shall not exceed 2.0ml ▪Shall be above 24.5^0C ▪Shall be not more than0.25percent by mass *Shall not differ from the declared value by more than the percent tolerance limits
X4	Cold test Emulsion stability Flash point Acidity Active ingredient (A.I.)	No turbidity No creaming 40^0c 0.0108 24.33	*No turbidity or separation of solid ▪Any separation including creaming at top and sedimentation at bottom shall not exceed 2.0ml ▪Shall be above 24.5^0C ▪Shall be not more than0.25percent by mass ▪Shall not differ from the declared value by more than the percent tolerance limits

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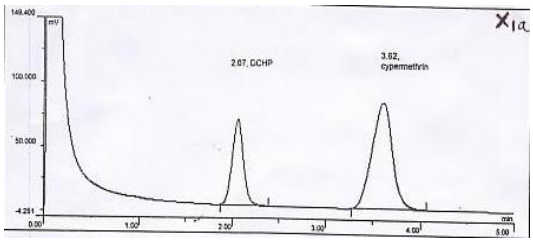
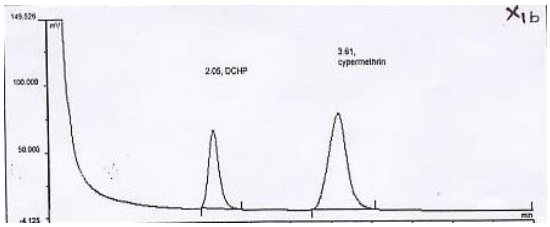
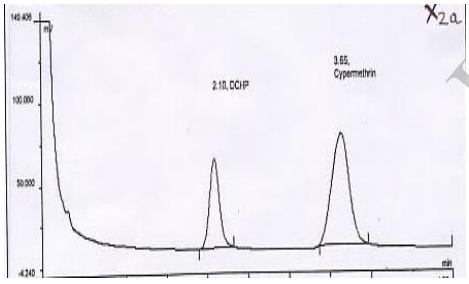
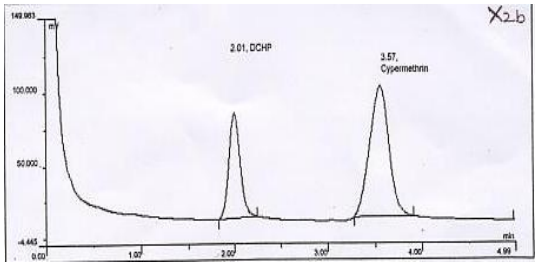
Sample X_1:



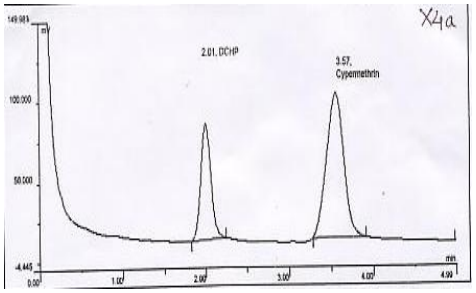


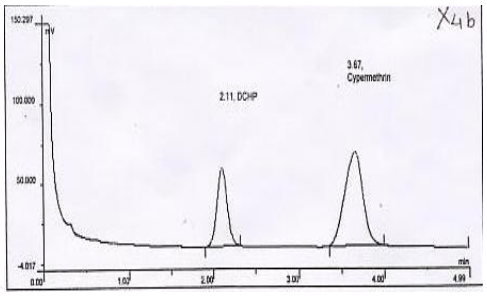
Sample X_2:





Sample X_4:





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1.3.2 B] Result of the various physical and chemical tests performed on different samples of chloropyrifos EC formulations collected are as follow:

Samples of chlorpyrifos (EC20)

	Test performed	Result	Standard Result
Y 1	Cold test Emulsion stability	No turbidity No creaming	▪No turbidity or separation of solid ▪Any separation including creaming at top and sedimentation at bottom shall not exceed 2.0ml

	Flash point Acidity Active ingredient(A.I.)	48^{0}c 0.043 19.27	▪Shall be above 24.5^{0}C ▪Shall be not more than0.25percent by mass ▪Shall not differ from the declared value by more than the percent tolerance limits
Y$_2$	Cold test Emulsion stability Flash point Acidity Active ingredient (A.I.)	No turbidity No creaming 42^{0}c 0.046 19.2179	▪No turbidity or separation of solid ▪Any separation including creaming at top and sedimentation at bottom shall not exceed 2.0ml ▪Shall be above 24.5^{0}C ▪Shall be not more than0.25percent by mass ▪Shall not differ from the declared value by more than the percent tolerance limits
Y$_3$	Cold test Emulsion stability	No turbidity No creaming	▪No turbidity or separation of solid ▪Any separation including creaming at top and sedimentation at bottom shall not exceed 2.0ml
	Flash point Acidity Active ingredient (A.I.)	50^{0}c 0.056 20.09	▪Shall be above 24.5^{0}C ▪Shall be not more than0.25percent by mass ▪Shall not differ from the declared value by more than the percent tolerance limits
Y$_4$	Cold test Emulsion stability Flash point Acidity Active ingredient (A.I.)	No turbidity No creaming 35^{0}c 0.044 19.98	▪No turbidity or separation of solid ▪Any separation including creaming at top and sedimentation at bottom shall not exceed 2.0ml ▪Shall be above 24.5^{0}C ▪Shall be not more than0.25percent by mass ▪Shall not differ from the declared value by more than the percent tolerance limits

Table 2: Showing results of physicochemical properties of chlorpyrifos (EC)

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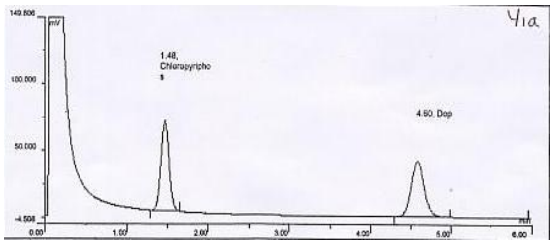
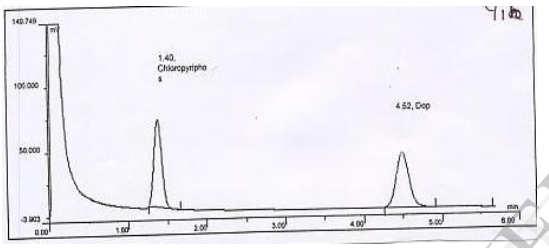
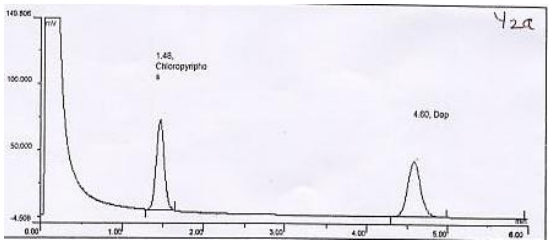
Results of Active Ingredient (A.I.) for samples Y_1, Y_2, Y_3 and Y_4 of chloropyrifos EC formulation are based on following spectrums obtained using GC-FID detector

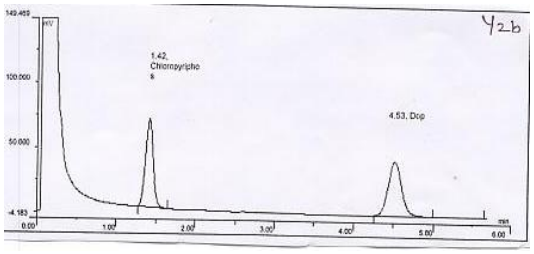
SampleY_1:



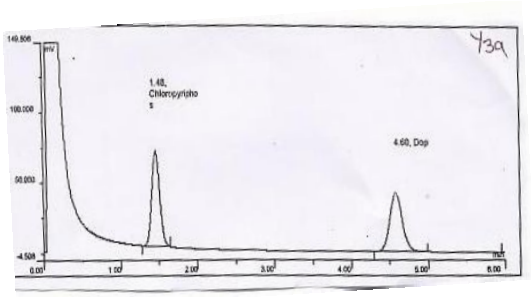


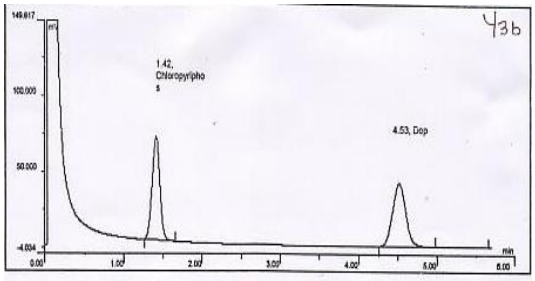
SampleY_2:



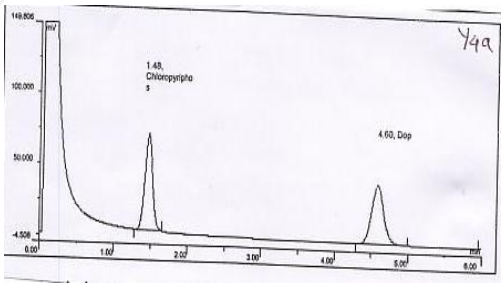


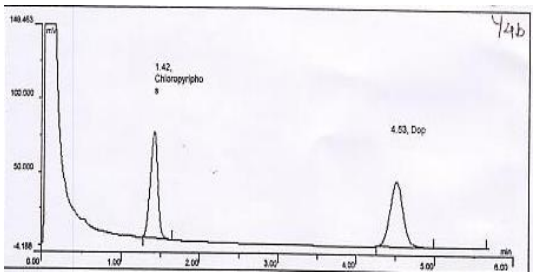
SampleY_3:





SampleY_4:





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1.4 Discussion:

Samples of EC (25) formulations of cypermethrin collected from market were tested as per guidelines given in BIS specification of EC formulations . There were four samples (X_1, X_2, X_3 and X_4) out of which two were from Indian manufacturing company and two were

form International manufacturing company.

All samples were up to the mark in their results for cold test but for emulsion stability test and acidity/alkalinity test except X_3 all others were up to the mark. All the samples had flash point above 24.5^0 c as per BIS specification. Even Active Ingredient in all samples were around 25 except for sample X_2 which was above 25 and for sample X_3 it was not determined as its emulsion stability test was not as per BIS specification.

Samples of EC (20) formulations of chloropyrifos, collected from market were tested as per guidelines given in BIS specification of EC formulations. There were four samples (Y_1, Y_2, Y_3 and Y_4) out of which two were from Indian manufacturing company and two were form International manufacturing company.

All samples were up to the mark in their results for physical tests such as cold test, emulsion stability test and flash point (which should be above 24.5^0c). Acidity/alkalinity test for all samples were up to the mark. In all samples active Ingredient was around 20.0 i.e. up to the mark.

1.5 Conclusion:

Physico-chemical properties of EC formulations of cypermethrin and chlorpyrifos which are commercially available are important in their selection to use against insect pests on crop. In the above studies as per BIS specification various national and international formulations available were tested for various physical and chemical tests and based on results of these test the formulation having better results for all tests performed on it was selected for application.

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